

JOURNAL OF THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS

ON ORGANIC CHEMISTRY.

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BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

The Asymmetric Carbon Atom. ERNST MOHR (*J. pr. Chem.*, 1903, [ii], 68, 369—384. Compare Rabe, *Abstr.*, 1901, i, 33; Aschan, *Abstr.*, 1903, ii, 2).—A theoretical paper. G. Y.

Action of Fuming Sulphuric Acid on *iso*Amyl Chloride. ROBERT A. WORSTALL (*J. Amer. Chem. Soc.*, 1903, 25, 932—935).—*iso*Amyl chloride was sulphonated by fuming sulphuric acid, and acicular crystals of the barium salt, $(\text{OH}\cdot\text{C}_5\text{H}_{10}\cdot\text{SO}_3)_2\text{Ba}\cdot 2\text{H}_2\text{O}$, were isolated. A concentrated aqueous solution of the salt, when boiled with dilute hydrochloric acid, did not develop a pink colour; no precipitate formed, and no odour of fusel oil was perceptible. The free acid, obtained from the lead salt by hydrogen sulphide, contained only a trace of sulphuric acid after being boiled with water. *iso*Amyl sulphate is possibly the initial product of the sulphonation, and, by further action, is converted into the hydroxysulphonic acid.

A. MCK.

Action of Water on Methylene Dibromide. KARL KLÖSS (*Monatsh.*, 1903, 24, 783—789. Compare Jeltekow, *Ber.*, 1873, 6, 558).—When heated with water at 150°, methylene dibromide is hydrolysed with formation of formaldehyde. After heating for 30 hours, the yield of formaldehyde is 89·1 per cent. of the theoretical; a 93·8 per cent. yield of formaldehyde is obtained on heating methylene dibromide with lead oxide and water for 26 hours at 150°. The author discusses the methods of estimating formaldehyde (see Legler, *Abstr.*, 1883, 1035; Lösekann, *Abstr.*, 1889, 1036; Eschweiler *Abstr.*, 1889, 1250; Blank and Finkenbeiner, *Abstr.*, 1899, ii, 188 820).

G. Y.

Nitromethane as a Solvent. LUDWIK BRUNER (*Ber.*, 1903, 36, 3297—3298).—[With J. KOZAK and G. MARIASZ.]—Pure nitromethane has a specific conductivity $k = 6.4 \times 10^{-7}$ inverse ohms at 18° . Very few electrolytes are soluble in nitromethane, but measurements are given for the molecular conductivity of tribromoacetic acid, antimony trichloride and tribromide, and mercury chloride in this solvent which show that it possesses ionising power, although the magnitude of this is very much less than might be anticipated from its high dielectric constant.

Chloropicrin has a specific conductivity 6.0×10^{-8} inverse ohms, and is less ionising than nitromethane. W. A. D.

Hydrates of Ethyl Alcohol. EUGÈNE VARENNE and L. GODEFROY (*Compt. rend.*, 1903, 137, 993—996).—Solutions of ethyl alcohol in water have been examined by means of a special form of constant pressure capillary viscosimeter. The curve representing the viscosity shows a principal maximum corresponding with the well-known hydrate $C_2H_5O, 3H_2O$, and also indicates the existence of hydrates with $2H_2O$ and $6H_2O$, and also, less distinctly, $3C_2H_5O, 2H_2O$ and $C_2H_5O, 22H_2O$. C. H. D.

Action of Organo-magnesium Compounds on Acetol and its Esters. ANDRÉ KLING (*Compt. rend.*, 1903, 137, 756—758).—The author has examined the behaviour of acetol and its esters with organo-magnesium compounds at low temperatures in order to determine whether they contain the $-CO-$ or $\begin{array}{c} \diagup \\ C \\ \diagdown \\ O \end{array}$ group (Abstr., 1903,

i, 138), since, under these conditions, compounds containing the former grouping yield a tertiary alcohol of the type $CRR'R''\cdot OH$ (Grignard, Abstr., 1900, i, 382), whilst compounds containing the latter grouping give secondary alcohols of the type $OH\cdot CHR\cdot CH_2X$, where X is a halogen radicle (Grignard, Abstr., 1903, i, 552). Acetol and its esters behave like ketonic compounds, yielding glycols, thus the *amyleneglycol*, $OH\cdot CMeEt\cdot CH_2\cdot OH$, was obtained from magnesium ethiodide and acetol acetate; *methyldiethylcarbinol*, $CMeEt_2\cdot OH$, and *amyleneglycol* from magnesium ethobromide and acetol acetate; magnesium methiodide and acetol acetate yielded the monoacetyl derivative of *butylglycol*, $OH\cdot CMe_2\cdot CH_2\cdot OH$, whilst acetol benzoate yielded *phenyldiethylcarbinol*, $CPhEt_2\cdot OH$, magnesium benzoate, and *amyleneglycol*. M. A. W.

Conversion of the $\alpha\gamma$ -Glycol from *iso*Butaldehyde into the Isomeric $\alpha\delta$ -Glycol. GUSTAV MOSSLER (*Monatsh.*, 1903, 24, 595—617. Compare Fossek, Abstr., 1884, 37, 832; Swoboda and Fossek, Abstr., 1891, 31; Franke, Abstr., 1896, i, 404).—The action of hydrobromic acid of sp. gr. 1.75 on Fossek's glycol and on the two oxides obtained by boiling the glycol with dilute sulphuric acid leads to the formation of $\alpha\delta$ -dibromo- $\beta\beta\delta$ -trimethylpentane. The reaction takes place most easily with the more volatile oxide; with the glycol, a small amount of the less volatile oxide is formed. In each case, there is obtained a liquid bromo-derivative which boils at 58 — 60° under 14 — 16 mm.

pressure. *αδ-Dibromo-ββδ-trimethylpentane*, $\text{CH}_2\text{Br}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{Br}$, crystallises from light petroleum in colourless, almost odourless, rhombic plates and prisms, melts at 68° , and boils at $102\text{--}103^\circ$ under 14 mm. pressure. When boiled with water, with dilute aqueous potassium carbonate solution, or with moist silver oxide (1 mol.) and water, the dibromide yields the oxide boiling at $120\text{--}122^\circ$. With an excess of silver oxide, the dibromide yields *ββδ-trimethylamylen-αδ-glycol*, $\text{OH}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{OH}$, which separates from ether in clusters of feathery crystals, melts at 86° , boils at $114\text{--}115^\circ$ under 13 mm., at $209\text{--}211^\circ$ under atmospheric pressure, and is isomeric with Fosse's glycol. The *diacetate*, formed by the action of silver acetate on the dibromide, is a colourless liquid, boils at $111\text{--}112^\circ$ under 11 mm., at $214\text{--}216^\circ$ under the ordinary pressure, and is hydrolysed to the glycol when boiled with 40 per cent. alcoholic potassium hydroxide.

The *αδ-glycol* is not acted on by neutral potassium permanganate solution at the laboratory temperature, but on warming it is completely decomposed. Alkaline potassium permanganate solution oxidises the glycol to a liquid substance which distils at $80\text{--}150^\circ$ under the ordinary pressure. Acid oxidising agents decompose the glycol.

When boiled with dilute sulphuric acid in a reflux apparatus or when heated with water at 180° , the *αδ-glycol* yields the more volatile oxide.

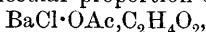
As suggested by Franke, the oxide boiling at $120\text{--}122^\circ$ must be represented by the constitutional formula $\begin{matrix} \text{CH}_2\cdot\text{CMe}_2 \\ \text{CMe}_2\cdot\text{CH}_2 \end{matrix} > \text{O}$, the oxide boiling at $260\text{--}262^\circ$ by the formula $(\text{C}_8\text{H}_{16})_2\text{O}_2$. G. Y.

Formation of Normal Diprimary Decylene Glycol (Decan- $\alpha\kappa$ -diol) by Reduction of Derivatives of Sebacic Acid. RUDOLF SCHEUBLE (*Monatsh.*, 1903, 24, 618—632).—Reduction of sebacamide with sodium and amyl alcohol leads to the formation of decamethylene $\alpha\kappa$ -glycol and a small amount of decamethylene- $\alpha\kappa$ -diamine.

Decamethylene $\alpha\kappa$ -glycol, $\text{OH}\cdot\text{CH}_2[\text{CH}_2]_8\cdot\text{CH}_2\cdot\text{OH}$, crystallises in long, white needles, melts at 70° , boils at 179° under 15 mm., or at 192° under 20 mm. pressure, and is soluble in ether, chloroform, or benzene, but less so in water or light petroleum. The *diacetate*, $\text{C}_{10}\text{H}_{20}(\text{OAc})_2$, is a colourless, crystalline mass, which melts at 25.5° , boils at 170.5° under 10 mm. pressure, and is easily soluble in organic solvents.

The glycol is oxidised to sebacic acid by potassium permanganate in neutral solution. G. Y.

Action of Chlorine on Barium Acetate. ALBERT COLSON (*Compt. rend.*, 1903, 137, 660—661).—When chlorine is passed into a solution of barium acetate in an acetic acid solution containing acetic anhydride at 12° , it forms a double salt, barium acetochloride, crystallising with one molecular proportion of acetic acid,



insoluble in acetic acid, but soluble in water. Curie has examined the barium precipitated from this compound with respect to

its radioactive properties, and finds that if it acquires radioactivity at all it is less than 1/20 that of uranium. M. A. W.

Hydrolysis and Synthesis of Fats by Platinum Black. HUGH NEILSON (*Amer. J. Physiol.*, 1903, 10, 191—200).—Platinum black accelerates the hydrolysis of ethyl butyrate as lipase does, only its action is slower. Its action, like that of lipase, increases with the increased concentration of the platinum, and is independent of the concentration of the ethyl butyrate. The action increases with temperature, reaching its maximum at 50°. Various poisons (thymol, salicylic acid, chloroform, phenol, &c.) affect the catalytic action of platinum as they do that of lipase. Sodium fluoride and hydrocyanic acid, however, have no effect. Platinum black also synthesises butyric acid and ethyl alcohol into ethyl butyrate; this is comparable to the "reversible" action of lipase. W. D. H.

Fats. ALFRED PARTHEIL and F. FÉRIÉ (*Arch. Pharm.*, 1903, 241, 545—569).—In the separation of fatty acids by means of the solubility or insolubility of their lead salts in benzene (Farnsteiner, *Zeit. Nahr. Chem.*, 1898, 390), the results are sometimes vitiated by the formation of a mixed lead salt, such as lead oleo-stearate. Obviously this might be avoided by using, not lead salts, but salts of a univalent metal; on this account, the solubility of the lithium salts of various fatty acids in water and alcohol of sp. gr. 0.797 was determined, in order to ascertain whether they could be utilised for the purpose. The acids employed were obtained by purifying the commercial specimens; they had the following constants:

| Acid. | M. p. | B. p. | n_D^{20} |
|--------------|-------|-------------------|------------------|
| Stearic..... | 70.5° | 238° under 17 mm. | 1.4325 at 71° |
| Palmitic ... | 62.5 | 219 " 17 " | 1.4284 " 74.5 |
| Myristic ... | 53.7 | 199 " 16 " | 1.4248 " 76.5 |
| Lauric | 43 | 177 " 16 " | 1.4236 " 76 |
| Oleic..... | — | 241 " 20 " | — — |

The salts were usually prepared by heating the alcoholic solution of the acid with a slight excess of lithium carbonate, and allowing the filtered solution to cool. The oleate, however, was prepared by mixing aqueous solutions of potassium oleate and lithium acetate, and crystallising the precipitate from alcohol. For the determination of the solubility, the salts were shaken for 48 hours with 200 c.c. of the solvent in bottles of Jena glass in a thermostat; the lithium salt was then estimated in aliquot parts of the filtrate. The results are tabulated below, the numbers indicating grams of the salt in 100 c.c. of the saturated solution.

| Lithium salt. | Water. | | Alcohol. | |
|---------------------------------------|--------|-------|----------|-------|
| | 18° | 25° | 18° | 25° |
| Stearate, $C_{17}H_{35}\cdot CO_2Li$ | 0.010 | 0.011 | 0.041 | 0.053 |
| Palmitate, $C_{15}H_{31}\cdot CO_2Li$ | 0.011 | 0.018 | 0.080 | 0.096 |
| Myristate, $C_{13}H_{27}\cdot CO_2Li$ | 0.023 | 0.023 | 0.184 | 0.210 |
| Laurate, $C_{11}H_{23}\cdot CO_2Li$ | 0.158 | 0.173 | 0.418 | 0.442 |
| Oleate, $C_{17}H_{33}\cdot CO_2Li$ | 0.067 | 0.132 | 0.908 | 1.009 |

Partly as a result of these determinations, the following method of

analysis was elaborated. About 1 gram of the fat is saponified with 15 c.c. of approximately $N/2$ alcoholic potassium hydroxide on the water-bath, the soap dissolved in 100 c.c. of 50 per cent. alcohol, and the solution neutralised with dilute acetic acid, phenolphthalein serving as the indicator. The lithium salts of the higher fatty acids are precipitated by adding a 10 per cent. solution of lithium acetate in 50 per cent. alcohol, the precipitate redissolved by warming to about 60° , and the solution allowed to cool, when lithium stearate, palmitate, and most of the myristate crystallise out. The crystals are filtered off, washed with 50 per cent. alcohol, dried, weighed roughly, dissolved in hot absolute alcohol, and the solution allowed to cool. The stearate and palmitate crystallise out, and are collected, dried at 100° , and weighed. The solution of myristate is evaporated, and the residue dried at 100° and weighed. Each residue is then decomposed with hydrochloric acid, and the liberated acid washed, dried, and titrated with alkali; thus in the one case the proportion between the stearic and palmitic acids is determined, in the other the myristic acid is identified.

The lithium salts that remain dissolved are converted into the lead salts, and these extracted with hot benzene. The insoluble residue is decomposed with hydrochloric acid and the proportion between the myristic and lauric acids determined by titration with alkali. The benzene solution is evaporated in a current of hydrogen, the residue decomposed with dilute hydrochloric acid, the liberated acids dissolved in alcohol, neutralised with potassium hydroxide, and converted into barium salts by means of 10 per cent. barium acetate solution. By extraction with ether saturated with water, the barium salts of the acids of the linoleic acid series are dissolved, and their weight, as well as that of the residual barium oleate, is determined.

In this way, the results tabulated below were obtained. The lard was of American origin. Of human fat, 7 samples were examined so far as regards the determination of the usual constants; these came from different parts of the body, and from both men and women. Two samples, one from a man, the other from a woman, were further analysed. Distinct amounts of acids of the linoleic series were found in human fat, in margarine, in lard, and also in butter. From the human fat, a liquid mixed glyceride, *dioleostearin*, was isolated.

| | Butter. | | Margarine. | Lard. | Human Fat. | |
|--|---------|------|------------|-------|------------|------|
| Iodine number | 35.2 | 36.4 | 69.5 | 65.8 | 57—66 | |
| Reichert-Meissl number... | 33.1 | 28.6 | — | — | 1.1—2.1 | |
| Köttstorfer number | — | — | — | — | 194—198 | |
| Hegner number | — | — | — | — | 94—96 | |
| Stearic acid..... | 6.6 | 10.5 | 19.1 | 8.4 | 12.3 | 12.4 |
| Palmitic acid | 18.2 | 14.5 | 6.1 | 4.5 | 29.2 | 27.0 |
| Myristic acid..... | 11.1 | 11.9 | 14.3 | 14.4 | — | — |
| Lauric acid..... | 16.4 | 14.9 | 7.0 | 11.7 | — | — |
| Unsaturated acids * | 30.7 | 32.6 | 47.1 | 54.0 | 48.6 | 53.0 |
| | 83.0 | 84.4 | 93.6 | 93.0 | 90.1 | 92.4 |
| * Of linoleic series | 5.4 | 4.1 | 20.3 | 10.0 | — | — |
| Iodine number (of unsaturated acids) | 115 | 112 | 148 | 122 | — | — |

C. F. B.

Theory of the Saponification Process. JULIUS LEWKOWITSCH (*Ber.*, 1903, 36, 3766—3768).—A reply to the criticisms of Balbiano (*Abstr.*, 1903, i, 547). T. M. L.

Behenolic Acid. M. HAASE and ALBERT STUTZER (*Ber.*, 1903, 36, 3601—3604).—*Behenolic chloride*, $C_{22}H_{39}OCl$, crystallises in needles and melts at 29—30°; it cannot be distilled in a vacuum without decomposition. The *ethyl ester*, $C_{24}H_{44}O_2$, forms minute, white needles, and melts at 15—16°. The *phenyl ester*, $C_{28}H_{44}O_2$, forms glistening, white, fatty scales and melts at 43°. The *anilide*, $C_{28}H_{45}ON$, forms monoclinic prisms and melts at 72°. The *acetanilide*, $C_{30}H_{47}O_2N$, crystallises from ethyl acetate in minute, white needles and melts at 45°. The *amide* forms glistening, fatty scales, melts at 90°, and, like behenolic acid, becomes pyroelectric when rubbed.

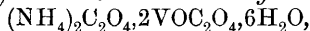
Monobromobrassicidic acid is produced in good yield when an ethereal solution of behenolic acid is saturated with hydrogen bromide in the cold and then gently warmed; it is reduced by sodium to brassidic acid, $C_{22}H_{40}O_2$, melting at 59°, whilst bromine water converts it into *dibromohydroxybehenic acid*, $C_{22}H_{42}O_3Br_2$, a colourless oil, solidifying to a crystalline mass which melted at 46—47°. By the action of alcoholic sodium hydroxide, the latter acid is converted into a *brominated glycidic acid*, $C_{22}H_{41}O_3Br$, which forms minute, silky needles and melts at 44°; dilute acids and alkalis convert this into *bromodihydroxybehenic acid*, $C_{22}H_{43}O_4Br$, which forms glistening, white scales and melts at 71°. T. M. L.

Chloro- and Bromo-hydroxybehenic Acids and their Transformation Products. D. WARMBRUNN and ALBERT STUTZER (*Ber.*, 1903, 36, 3604—3606).—Chloro- and bromo-hydroxybehenic acids are readily obtained in a pure state by the action of chlorine or bromine on the sodium salts of erucic or brassidic acids, sodium haloid being eliminated. The derivative from erucic acid is hydrolysed by sodium hydroxide, forming a glycidic acid, $C_{22}H_{42}O_3$, separating from ether as a fine, white powder melting at 64°, insoluble in water, but dissolving readily in organic solvents. Its salts are amorphous and dissolve in alcohol. Ammonia reacts with the sodium salt in alcoholic solution at 140° to form *aminohydroxybehenic acid*, $C_{22}H_{45}O_3N$, a white, amorphous powder melting at 86°, dissolving sparingly in alcohol, readily in glacial acetic acid. Acetic anhydride forms an *anhydride* of *diacet-oxybehenic acid*, $C_{26}H_{48}O_6$, crystallising in small needles melting at 63°. Heating with potassium hydroxide solution at 170° further hydrolyses it to dihydroxybehenic acid melting at 99°, and identical with that obtained by Albitzky (*Abstr.*, 1899, i, 862). The chloro-derivative from brassidic acid reacts in a similar manner, forming a glycidic acid separating from alcohol in crystals melting at 71° and dissolving in ether. Further hydrolysis gives rise to the dihydroxybehenic acid melting at 133°, which also results from the direct oxidation of erucic acid. C. H. D.

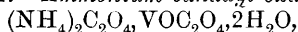
Oxidation of Oxalic Acid by Free and Combined Oxygen. WILLEM P. JORISSEN and LODIEWYK T. REICHER (*Zeit. Farb. Text.-Chem.*, 1903, 2, 431—435).—Mainly a review of previous work on the

subject. The oxidation of oxalic acid solutions by gaseous oxygen (compare Richardson, *Trans.*, 1894, 65, 450; Jorissen, *Abstr.*, 1899, 739; Jorissen and Reicher, *Abstr.*, 1900, ii, 200), hydrogen peroxide, potassium permanganate, and chromic acid (Werner, *Trans.*, 1887, 51, 388; Prudhomme, *Abstr.*, 1903, ii, 430) is discussed. Werner's equation, $\text{H}_2\text{Cr}_2\text{O}_7 + 9\text{H}_2\text{C}_2\text{O}_4 = \text{H}_6\text{Cr}_2(\text{C}_2\text{O}_4)_6 + 7\text{H}_2\text{O} + 6\text{CO}_2$, involving the formation of chromoxalic acid in the oxidation of oxalic acid by chromic acid is confirmed by quantitative measurements. In presence of an excess of sulphuric acid and chromium sulphate, the oxidation in this case is a reaction of the first order. The remainder of the paper deals with the oxidation of oxalic acid solutions by chromic acid in presence of indigotin (compare von Georgievics, *Zeit. Farb. Text.-Chem.*, 1903, 2, 200).
W. A. D.

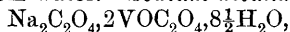
Compounds of Quadrivalent Vanadium. II. IWAN KOPPEL and R. GOLDMANN (*Zeit. anorg. Chem.*, 1903, 36, 281—301. Compare *Abstr.*, 1903, ii, 551).—*Ammonium divanadyl oxalate*,



prepared (1) by melting together oxalic acid and ammonium metavanadate and then extracting the mass with alcohol, or (2) by dissolving ammonium metavanadate (2 mols.) and oxalic acid (4 mols.) in water and then adding acetone, forms greenish-blue crystals and is easily soluble in water. *Ammonium vanadyl oxalate*,



prepared from ammonium metavanadate (2 mols.), oxalic acid (4 mols.), and ammonium oxalate (1 mol.), is distinguished from the divanadyl oxalate by being more readily crystallisable and by its blue colour. *Potassium divanadyl oxalate*, $\text{K}_2\text{C}_2\text{O}_4, 2\text{VOC}_2\text{O}_4, 4\text{H}_2\text{O}$, is blue, and can be crystallised from water. *Sodium divanadyl oxalate*,

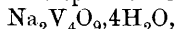


separates in dark blue clusters of needles.

Ammonium vanadyl thiocyanate, $(\text{NH}_4)_2\text{VO}(\text{CNS})_4, 5\text{H}_2\text{O}$, prepared from an aqueous solution of its components by precipitation with ethyl acetate, forms rhombic crystals [$a:b:c=0.991:1:0.607$]. *Potassium vanadyl thiocyanate*, $\text{K}_2\text{VO}(\text{CNS})_4, 5\text{H}_2\text{O}$, is isomorphous with the ammonium salt [$a:b:c=0.9163:1:0.5469$]. The corresponding sodium salt could not be isolated.

A quantitative method of separating vanadium, based on the solubility of ammonium vanadyl thiocyanate in a mixture of 9 parts of ether and 1 part of amyl alcohol, is described.

Ammonium vanadite, $(\text{NH}_4)_2\text{V}_4\text{O}_9, x\text{H}_2\text{O}$, prepared by the addition of a boiling solution of a vanadyl salt to ammonia, separates in glistening brown needles or scales. Its aqueous solution is readily oxidised on exposure to the atmosphere. *Sodium vanadite*,



forms golden needles or scales. *Potassium vanadite*, $\text{K}_2\text{V}_4\text{O}_9, 4\text{H}_2\text{O}$, and *barium vanadite*, $\text{BaV}_4\text{O}_9, 4\text{H}_2\text{O}$, are described, but silver vanadite could not be prepared.
A. McK.

Use of Magnesium Amalgam in Organic Chemistry. LOUIS MEUNIER (*Compt. rend.*, 1903, 137, 714—716. Compare *Abstr.*, 1902, i, 335).—Diphenylmethane is conveniently prepared by the action of

magnesium amalgam on a mixture of benzyl chloride and bromobenzene. Ethyl malonate is not attacked by magnesium, even on warming, but when dissolved in benzene the reaction occurs readily, the magnesium entering the methylene group of the ester. The compound thus formed reacts with ethyl iodide, forming ethyl ethylmalonate, which may be converted into ethyl diethylmalonate by treatment with magnesium ethoxide and subsequent action of ethyl iodide. Magnesium ethyl iodide acts on the methylene group of ethylmalonate, hydrolysis of the ester taking place when an excess of the magnesium compound is used. C. H. D.

Action of Sulphur Chloride on Ethyl and Methyl Malonates. HEINRICH WOLFF and A. OTT (*Ber.*, 1903, 36, 3721—3726).—Ethyl malonate reacts with sulphur chloride in presence of aluminium chloride, forming a gelatinous mass of *ethyl dithiomalonate*, $S_2[CH(CO_2Et)_2]_2$, which separates from hot acetone as an almost colourless syrup, converted by repeated precipitation with water from alcoholic solution into rosettes of small needles melting at 131° , and very sparingly soluble in organic solvents with the exception of carbon disulphide. The syrupy form is more readily soluble in all solvents, but shows no difference in composition or molecular weight. Phenylhydrazine decomposes the sulphide with formation of sulphur and hydrogen sulphide.

Methyl malonate reacts with sulphur chloride in presence of aluminium chloride at $70-80^\circ$. The crystalline product is extracted with acetone and recrystallised from alcohol. *Methyl trithiomalonate*, $S_3[CH(CO_2Me)_2]_2$, forms white, flexible needles with green lustre, melting at 167° and dissolving readily in benzene, carbon disulphide, glacial acetic acid, or hot acetone, insoluble in water or ether. The mother-liquor deposits a further small quantity of the same substance after 3—4 weeks. The remainder of the syrup is repeatedly dissolved in alcohol and precipitated with water, and then yields a clear, viscous syrup, which deposits a small quantity of *methyl thiomalonate*, $S[CH(CO_2Me)_2]_2$, as white rhombohedra, melting at 122° and dissolving readily in ether, benzene, glacial acetic acid, or alcohol, less soluble in acetone; it may also be prepared by the action of sulphur dichloride on methyl malonate. Both the mono- and trithio-compounds react with phenylhydrazine, forming *thiomalonic hydrazide*, $C_{30}H_{30}O_4N_8S$, crystallising from 60 per cent. alcohol in glistening, white prisms melting at 120° . This reaction can only be explained by assuming the grouping $:CH \cdot S \cdot CH:$ in the trithio-ester, the grouping $:CH \cdot S \cdot S \cdot S \cdot CH:$,



suggested by Angeli and Magnani (*Abstr.*, 1894, i, 547) being excluded. C. H. D.

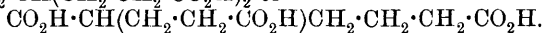
Preparation of Adipic Acid. LOUIS BOUVEAULT (*Bull. Soc. chim.*, 1903, [iii], 29, 1038—1043).—The author found that a solution of sodium methyl succinate, prepared by the addition of a solution of sodium methoxide in methyl alcohol to finely powdered succinic

anhydride suspended in methyl alcohol, when electrolysed, furnished 70 per cent. of the theoretical amount of methyl adipate. The apparatus employed consisted of a two litre flask, fitted with an india-rubber stopper carrying an iron wire in contact with a layer of mercury (constituting the negative electrode) in the flask. The positive electrode was a spiral tube of platinum, through which a rapid current of cold water circulated. The electrolyte had a resistance of four ohms, and a current of 7 to 8 amperes and 25 to 30 volts was necessary to effect the change. Sodium ethyl succinate dissolved in ethyl alcohol proved to be too highly resistant to permit of the preparation of ethyl adipate by this process, but aqueous solutions of the salt when electrolysed gave small yields of ethyl adipate.

Methyl adipate is a colourless liquid of unpleasant odour; it boils at 115° under 13 mm. pressure, crystallises when cooled to 0° , and melts at 8° .

α -Hydroxysuberic and $\alpha\beta$ -dihydroxysebacic acids, prepared by Weger's process (Abstr., 1894, 359), can be separated readily from the by-products of the reaction by precipitation as the cupric salts and regeneration of the acids from these by the action of hydrogen sulphide on the salts suspended in water. T. A. H.

By-products of the Electrolytic Preparation of Adipic Acid. LOUIS BOUVEAULT (*Bull. Soc. chim.*, 1903, [iii], 29, 1043—1046. Compare preceding abstract).—When sodium ethyl succinate is electrolysed in aqueous solution, carbon dioxide is evolved and the surface of the electrolyte becomes covered with an oily layer. When the reaction liquid is extracted with ether and the residue left after evaporating off the solvent is distilled under reduced pressure, four fractions are obtained. The first of these consists of ethyl propionate with a small quantity of ethyl acrylate (compare Brown and Walker, Abstr., 1891, 1192, 1193), the second of ethyl β -hydroxypropionate (Klimenko and Rufalowicz, *J. Russ. Phys. Chem. Soc.*, 1894, 26, 413), probably formed by the combination of ethyl acrylate (1 mol.) with water (1 mol.); the third is principally ethyl adipate, whilst the fourth is the *triethyl ester* of an acid having the formula $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$ or

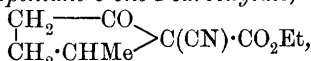


It boils at 195 — 205° under 10 mm. pressure and has a sp. gr. 1.072 at $0^{\circ}/4^{\circ}$. The free *acid* is very soluble in water and crystallises with difficulty.

The products of the electrolysis of sodium methyl succinate, dissolved in methyl alcohol, may be similarly separated into three fractions, the first consisting of methyl adipate, the second of *methyl hydrogen succinate*, which is crystalline, melts at 57 — 58° , boils at 151° under 20 mm. pressure, and is readily soluble in water and organic solvents. This ester is not produced during electrolysis, but is formed by the fractional distillation of the crude oil. The third portion is probably the *trimethyl ester* of the acid $\text{C}_9\text{H}_{14}\text{O}_6$, similarly obtained from sodium ethyl succinate. It is a colourless oil, boils at 194° under 20 mm. pressure, and has a sp. gr. 1.132 at $0^{\circ}/4^{\circ}$. T. A. H.

Synthesis of β -Methyladipic Acid. WILLIAM A. NOYES and IRVING J. COX (*J. Amer. Chem. Soc.*, 1903, 25, 1093—1096).—It has been shown by Noyes (Abstr., 1901, i, 631) that ethyl 1-cyano-2:2-dimethylcyclopentane-5-one-1-carboxylate is decomposed by sodium hydroxide with formation of the sodium salts of malonic and hydroxy-isohexoic acids. In order to determine whether this reaction is of general application, an attempt has been made to prepare a similar compound containing only one methyl group.

By the condensation of ethyl γ -chlorovalerate with ethyl cyanoacetate in presence of sodium ethoxide, a small quantity of a crystalline substance was obtained which melts at 185° and is probably ethyl 1-cyano-2-methylcyclopentane-5-one-1-carboxylate,



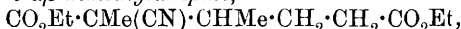
but the amount was insufficient for further examination.

Ethyl α -cyano- β -methyladipate,



obtained by the condensation of ethyl bromovalerate with ethyl cyanoacetate, boils at $175\text{--}185^\circ$ under 20 mm. pressure. When this ester is hydrolysed with alcoholic sodium hydroxide, β -methylbutane- α,α -tricarboxylic acid is produced, which crystallises in plates, melts and decomposes at $127\text{--}128^\circ$, and when heated at 200° is converted into β -methyladipic acid; its calcium salt crystallises with $3\text{H}_2\text{O}$.

Ethyl α -cyano- $\alpha\beta$ -dimethyladipate,



prepared by the action of methyl iodide on ethyl cyanomethyladipate in presence of sodium ethoxide, boils at $181\text{--}194^\circ$ under 29 mm. pressure, and, on hydrolysis, yields $\alpha\beta$ -dimethylbutane- α,α -tricarboxylic acid, which forms white, pearly crystals, melts at 159° , and if heated at 200° is converted into $\alpha\beta$ -dimethyladipic acid. E. G.

Preparation of Ethyl Glutaconate. EDMOND E. BLAISE (*Bull. Soc. chim.*, 1903, [iii], 29, 1012—1015. Compare Abstr., 1903, i, 400 and 548).—Sodium acetonedicarboxylate, prepared by Jerdan's method (*Trans.*, 1899, 75, 809), is reduced by sodium amalgam (von Pechmann and Jenisch, Abstr., 1891, 147) and the resulting β -hydroxyglutaric acid freed from associated β -hydroxybutyric acid by conversion into the ethyl ester and fractionation of this under reduced pressure.

When β -hydroxyglutaric acid is treated with acetyl chloride, it is converted into the anhydride of β -acetoxyglutaric acid; ethyl β -hydroxyglutarate, on the other hand, either by acetic anhydride or acetyl chloride is converted into ethyl β -acetoxyglutarate, which, when distilled under atmospheric pressure, is decomposed into acetic acid and ethyl glutaconate. The yields of ethyl β -hydroxyglutarate and ethyl glutaconate obtained by this process amounted to 43 and 30 per cent. respectively of the weight of acetonedicarboxylic acid used.

T. A. H.

Optical Rotatory Power of Glutamic Acid. KARL ANDRÁK (*Zeit. Ver. deut. Zuckerind.*, 1903, 572, 948—958).—The author has

studied the influence of foreign substances on the rotation of pure glutamic acid prepared from molasses residues and having $[\alpha]_D + 12.04^\circ$ in 1 per cent. solution at 20° . Weak acids such as boric, acetic, &c., are almost entirely without influence. Increasing amounts of strong acids cause a continuous increase of the specific rotation which tends towards a maximum. The addition of bases first changes the dextro- into a lævo-rotation, which attains its highest numerical value with the formation of the acid salt; further quantities of base convert the lævo- back into a dextro-rotation. With lead hydroxide, however, no change in sign of the rotation takes place. Basic lead acetate, in small quantities, diminishes the rotation, and in larger quantities changes it to a lævo-rotation which increases considerably as the amount of acetate is increased. Betaine, in small proportions (1.5 per cent.), has no effect on the rotation. T. H. P.

Oxalacetic Acid. LOUIS J. SIMON (*Compt. rend.*, 1903, 137, 855—857).—The author shows that it is possible to obtain oxalacetic acid from the ester by hydrolysis. The freshly distilled ester (one part) is mixed with concentrated hydrochloric acid (four parts) and shaken to assist solution. After the lapse of forty-eight hours at the ordinary temperature, the reaction is complete. Oxalacetic acid obtained by this method is identical with that prepared in other ways. It can be distinguished from a mixture of acetic and oxalic acids by the following reactions: aqueous or alcoholic ferric chloride gives an intense red coloration; sodium nitroprusside and potassium hydroxide provoke a deep red colour which changes to violet and finally disappears on the addition of acetic acid; ammonia and sodium nitroprusside impart a blue colour to the solution of the acid. S. S.

Nitric Esters of Hydroxy-acids. H. DUVAL (*Compt. rend.*, 1903, 137, 571—573).—*Malic acid nitrate*, $\text{CO}_2\text{H}\cdot\text{CH}(\text{O}\cdot\text{NO}_2)\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, prepared similarly to glycollic acid nitrate (*Abstr.*, 1903, i, 603) by dissolving malic acid in a mixture of nitric acid of sp. gr. 1.45 and concentrated sulphuric acid, crystallises from a very small quantity of water in stellate clusters of white needles, which are not deliquescent; it melts and decomposes at 115° ; dissolves in water, alcohol, ether, or acetic acid, and is insoluble in benzene or light petroleum.

Glyceric acid dinitrate, $\text{NO}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}(\text{O}\cdot\text{NO}_2)\cdot\text{CO}_2\text{H}$, is precipitated at -12° from a solution of glyceric acid in equal parts of fuming nitric and concentrated sulphuric acids; it crystallises from a mixture of ether and light petroleum (1 : 2) or from benzene in white crystals which decompose when kept at 117° for a few moments; it dissolves readily in water, alcohol, or ether, and is insoluble in light petroleum, chloroform, or carbon tetrachloride. M. A. W.

Solubility of Salts of the Alkaline Earths with Organic Acids in Acetic Acid. WALTER HERZ and G. MUHS (*Ber.*, 1903, 36, 3715—3718).—The solubility of calcium, strontium, and barium tartrates and oxalates in acetic acid of various concentrations was determined at 26 — 27° . In all cases, the solubility is least in con-

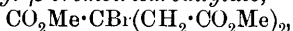
centrated acetic acid, and exhibits a maximum between 2.5- and 3.5-normal, corresponding with the maximum of electrical conductivity between these concentrations. The purified salts, dried in a vacuum-desiccator, have the composition $\text{CaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$; $\text{SrC}_4\text{H}_4\text{O}_6 \cdot 3\text{H}_2\text{O}$; $\text{BaC}_4\text{H}_4\text{O}_6$; $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$; $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$; $\text{BaC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$. C. H. D.

Cholic Acid. LODOVICO BECCARI (*Atti R. Accad. Torino*, 1903, 38, 882—893).—Cholic acid crystallised from alcohol was obtained in the form of tetrahedra or octahedra having the composition $\text{C}_{24}\text{H}_{40}\text{O}_5 \cdot \text{C}_2\text{H}_6\text{O}$, which lose their alcohol of crystallisation at 110—115° and melt at 197°. The crystalline modification of the acid containing $1\text{H}_2\text{O}$, obtained by crystallising the moist acid from ether, is best dehydrated by heating for 2—4 hours at 115° under 600 mm. pressure. The anhydrous hexagonal prisms melting at 197° can only be prepared by boiling a saturated aqueous solution directly over the flame. The anhydrous acid has the molecular weight 407 in boiling acetone and 425 in boiling alcohol.

The bromo-derivative, $\text{C}_{18}\text{H}_{25}\text{O}_3\text{Br}$, obtained by the cautious addition of bromine to the dry powdered acid, separates from alcohol or ether in small, colourless prisms which melt and decompose at about 130° and dissolve in alkali carbonate solutions, by which, and also by alkali hydroxides, they are decomposed. T. H. P.

Synthesis of Tartaric Acid. SILVESTRO ZINNO (*L'Orosi*, 1902, 25, 293—301).—After enumerating the known methods of synthesising tartaric acid and also some new ones, which are, however, only of theoretical significance, the author goes on to describe experiments made with the view of arriving at a method of synthesis which could be made use of in practice. He finds that the best results are obtained by just saturating glyceric acid of 26° B. at 15°, quite free from nitric acid, with potassium hydroxide solution of sp. gr. not greater than 1.134, the potassium glycerate thus formed being then treated with carbon dioxide under a pressure of 3 atmospheres. In this way, cream of tartar is obtained. This synthesis necessitated a means of preparing glyceric acid cheaply, which can be effected by heating a solution of glycerol, acidified with nitric acid, with lead dioxide or minium until decomposition is complete. The reactions in the two cases are expressed by the equations: (1) $2\text{PbO}_2 + 2\text{C}_3\text{H}_8\text{O}_3 + 4\text{HNO}_3 = \text{Pb}(\text{NO}_3)_2 + 5\text{H}_2\text{O} + \text{Pb}(\text{C}_3\text{H}_5\text{O}_4)_2 + \text{NO} + \text{NO}_2$; (2) $\text{Pb}_3\text{O}_4 + 2\text{C}_3\text{H}_8\text{O}_3 + 6\text{HNO}_3 = 2\text{Pb}(\text{NO}_3)_2 + \text{Pb}(\text{C}_3\text{H}_5\text{O}_4)_2 + 6\text{H}_2\text{O} + 2\text{NO}$. T. H. P.

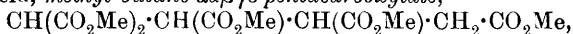
Action of Methyl Chlorotricarballylate on Ethyl Sodiomalonate and Ethyl Sodioacetoacetate. W. BERTRAM (*Ber.*, 1903, 36, 3291—3297).—Methyl aconitate, although failing to interact additively with hydrogen chloride, readily combines with hydrogen bromide to form methyl β -bromotricarballylate,



which crystallises from ether in colourless needles, melts at 98—99°, and is easily decomposed on heating.

When methyl β -chlorotricarballylate, $\text{CO}_2\text{Me} \cdot \text{CCl}(\text{CH}_2 \cdot \text{CO}_2\text{Me})_2$, is condensed with methyl sodiomalonate (2 mols.) and the crystalline

sodium compound obtained carefully decomposed at 0° with hydrochloric acid, *methyl butane- $\alpha\beta\gamma\delta$ -pentacarboxylate*,



is obtained; it crystallises from methyl alcohol and benzene in colourless needles and melts at $95-96^{\circ}$. The analogous *trimethyl diethyl ester*, $\text{CH}(\text{CO}_2\text{Et})_2 \cdot \text{CH}(\text{CO}_2\text{Me}) \cdot \text{CH}(\text{CO}_2\text{Me}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$, prepared by using ethyl instead of methyl sodiomalonate, crystallises from dilute alcohol in leaflets and melts at $57-58^{\circ}$. Both salts on hydrolysis give *n*-butane- $\alpha\beta\gamma\delta$ -tetracarboxylic acid (Auwers, Abstr., 1893, i, 253; 1894, i, 362). As the esters of a pentacarboxylic acid yielding *isobutanetetracarboxylic acid*, $\text{CO}_2\text{H} \cdot \text{C}(\text{CH}_2 \cdot \text{CO}_2\text{H})_3$, are not formed in the foregoing condensations, it is most probable that the sodiomalonic esters really react additively with methyl aconitate, formed from the chlorotricarballylate by the loss of hydrogen chloride. In like manner, methyl β -chlorotricarballylate and ethyl sodioacetoacetate give rise to *trimethyl ethyl α -acetyl-*n*-butane- $\alpha\beta\gamma\delta$ -tetracarboxylate*, $\text{CO}_2\text{Et} \cdot \text{CHAc} \cdot \text{CH}(\text{CO}_2\text{Me}) \cdot \text{CH}(\text{CO}_2\text{Me}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$, which crystallises from methyl alcohol and melts at 102° . W. A. D.

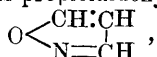
Citric Acid. JULIUS MEYER (*Ber.*, 1903, 36, 3599—3601).—It has been suggested by Buchner and Witter (Abstr., 1892, 824) that there is a difference between the properties of aqueous solutions of hydrated and anhydrous citric acid, since the latter usually deposits anhydrous crystals. The hydrated acid separates, however, when a crystal of this form is added to the solution, and no difference can be detected between the densities or the conductivities of solutions prepared from the hydrated and the anhydrous acid. T. M. L.

New Method of Preparation of Aldehydes. LOUIS BOUVEAULT (*Compt. rend.*, 1903, 137, 987—989).—Béris has shown (this vol., i, 15) that amides react with magnesium alkyl haloids, but that the negative character of the hydrogen atoms in the NH_2 group causes a secondary reaction, which entirely prevents the formation of aldehydes in the case of formamide. Disubstituted derivatives of formamide, however, react normally according to the equation $\text{NRR}' \cdot \text{CHO} + \text{MgXR}'' = \text{NRR}' \cdot \text{CHR}'' \cdot \text{OMgX}$, decomposing with water and dilute acids into $\text{R}'' \cdot \text{CHO}$, NHRR' , and $\text{MgX} \cdot \text{OH}$. This method may be employed in the synthesis of a large number of aldehydes. C. H. D.

Interaction between Formaldehyde and Silver Nitrate in presence of Strong Bases. LUDWIG VANINO (*Ber.*, 1903, 36, 3304—3305).—Silver is quantitatively separated from a solution containing silver nitrate (4 mols.), sodium hydroxide (6 mols.), and formaldehyde (2 mols.), whilst the filtrate contains sodium formate. The separation of silver is complete only when the sodium hydroxide is in excess. When both sodium hydroxide and formaldehyde are in large excess, a considerable evolution of hydrogen takes place; the action is catalytic. A. McK.

Propargylaldehyde [Propiolaldehyde] and Phenylpropargylaldehyde [Phenylpropiolaldehyde]. LUDWIG CLAISEN [and, in part, with PELTZ, STREITWOLF, and A. THOMASCHESKY] (*Ber.*, 1903, 36, 3664—3373. Compare Abstr., 1898, i, 422).—The yield of these aldehydes by the action of alkali hydroxides on the corresponding acetals is not good, but in most reactions the acetals themselves may be employed in place of the aldehydes.

Hydroxylamine transforms propiolaldehyde into isooxazole,



and not into the isomeric oxime. It is a colourless, mobile liquid, with a strong odour of pyridine, boils at 95—95.5° under 760 mm. pressure, and has a sp. gr. 1.0843 at 14°. It forms a compound, $2\text{C}_3\text{H}_3\text{ON}, \text{PtCl}_4$, in the form of yellow crystals, and a compound, $\text{C}_3\text{H}_3\text{ON}, \text{CdCl}_2$, as a colourless, crystalline powder. Alcoholic soda, or potassium ethoxide, transforms the isooxazole into the alkali salt of cyanovinyl alcohol, $\text{ONa}\cdot\text{CH:CH}\cdot\text{CN}$, which reacts with benzenediazonium chloride yielding a compound, $\text{CHO}\cdot\text{C}(\text{CN})\cdot\text{N}\cdot\text{NPh}$, in the form of brownish-red, flat prisms melting at about 168°. The corresponding anilide, $\text{NPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CN}$ or $\text{NPh}\cdot\text{CH:CH}\cdot\text{CN}$, is colourless and melts at 124°.

Solutions of hydrazine sulphate and of phenylhydrazine hydrochloride convert the acetal of propiolaldehyde into pyrazole and 1-phenylpyrazole (compare Albiano, Abstr., 1890, 797). Aniline forms an additive compound, $\text{CH:CH}(\text{OH})\cdot\text{NPh}$, with the aldehyde; it melts at 122—123°, and, when boiled with an aqueous alcoholic solution of aniline hydrochloride, yields the compound $\text{C}_{15}\text{H}_{14}\text{N}_2\cdot\text{HCl}$, probably the hydrochloride of the diamide of β -hydroxyacetaldehyde, $\text{NPh}\cdot\text{CH:CH}\cdot\text{CH}\cdot\text{NPh}$. The same product may be obtained by boiling the acetal of propiolaldehyde with an aqueous alcoholic solution of aniline hydrochloride. The free base crystallises in plates, melts at 115°, and yields sparingly soluble salts. When boiled with aqueous hydroxylamine hydrochloride, it yields isooxazole.

When heated with sodium ethoxide at 100°, the acetal of propiolaldehyde combines with a molecule of ethyl alcohol yielding β -ethoxyacetaldehyde acetal, $\text{OEt}\cdot\text{CH:CH}\cdot\text{CH}(\text{OEt})_2$, as a colourless oil distilling at 190—193°. The same compound is obtained when Fischer and Giebe's ethoxybromopropiondehydracetal (Abstr., 1898, i, 168) is warmed with alcoholic potash. The β -ethoxy-acetal, when shaken with water, loses a molecule of alcohol and yields malondialdehyde, or the tautomeric β -hydroxyacetaldehyde, which forms a phenylazo-derivative, $(\text{C}_3\text{H}_2\text{O}_2)\cdot\text{N}\cdot\text{NPh}$, melting at 116°.

Phenylpropiolaldehyde and ethyl malonate yield ethyl phenylpropionylidenemalonate, $\text{CPh}\cdot\text{CH:CH}\cdot\text{C}(\text{CO}_2\text{Et})_2$, which, on warming with sulphuric acid, passes into ethyl 6-phenyl-2-pyrone-3-carboxylate, $\text{CO}_2\text{Et}\cdot\text{C} \begin{array}{c} \diagup \text{CO—O} \\ \diagdown \text{CH}\cdot\text{CH} \end{array} \text{CPh}$, melting at 107—108°.

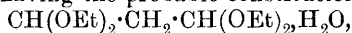
The oxime of phenylpropiolaldehyde melts at 108° and, on treatment with acetic anhydride, yields the nitrile of phenylpropionic acid.

A small amount of alkali transforms it into the isomeric α -phenyl-*isooxazole*; alcoholic sodium ethoxide at the ordinary temperature gives rise to cyanoacetophenone (Claisen and Stock, Abstr., 1891, 451).

γ -Substituted *isooxazoles* are somewhat more stable towards alkali hydroxides, but ultimately furnish acetic acid and a nitrile, γ -phenyl-*isooxazole* yielding benzonitrile and acetic acid. J. J. S.

Oxidation of β -Hydroxypropionacetal. CARL D. HARRIES (*Ber.*, 1903, 36, 3658—3659).—A preliminary notice occasioned by the intimation of the publication of Claisen (preceding abstract). Just as methyl alcohol is oxidised by ozone to formaldehyde (Harries, Abstr., 1903, i, 605), β -hydroxypropionacetal, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$, suffers oxidation to the half acetal of malondialdehyde, $\text{CHO}\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$.

The syrup, obtained by the oxidation of β -hydroxypropionacetal, reduced Fehling's solution when warmed gently, and yielded an oily phenylhydrazone; it could not, however, be distilled without decomposition until it had been converted into the acetal by Claisen's method, when a compound having the probable constitution,



was obtained. On hydrolysis, this substance formed a phenylhydrazone melting above 200° , possibly malondialdehyde phenylhydrazone. A. McK.

Action of Mixed Organomagnesium Compounds on Amides. New Method of Preparing Ketones. CONSTANTIN BÉIS (*Compt. rend.*, 1903, 137, 575—576).—Condensation between mixed organomagnesium compounds and acid amides occurs either at the NH_2 group or at both the CO and the NH_2 groups. Condensations of the latter type give a product which is decomposed by water yielding a ketone, according to the equations:



(2) $\text{CRR}'(\text{NHMgX})\cdot\text{OMgX} + 2\text{H}_2\text{O} = \text{NH}_2\cdot\text{CRR}'\cdot\text{OH} + \text{MgX}_2 + \text{Mg}(\text{OH})_2$; (3) $\text{NH}_2\cdot\text{CRR}'\cdot\text{OH} = \text{R}\cdot\text{CO}\cdot\text{R}' + \text{NH}_3$, where X is a halogen radicle. The following ketones were thus prepared: methyl ethyl ketone from acetamide and magnesium etho-bromide or -iodide; diethyl ketone from propionamide and magnesium ethobromide; methyl propyl ketone from butyramide and magnesium methiodide; ethyl *isobutyl* ketone from *isovaleramide* and magnesium ethobromide; acetophenone from benzamide and magnesium methiodide; phenyl ethyl ketone from benzamide and magnesium ethiodide. The yield varies from 20 to 50 per cent., increasing with the complexity of the organic residue of the acid amide, thus, acetamide reacts only feebly with the organomagnesium compounds, and formamide does not react at all in the sense of the above equations. M. A. W.

Diacetone Alcohol and Mesityl Oxide. MORITZ KOHN (*Monatsh.*, 1903, 24, 765—772).—Diacetone alcohol [dimethylacetonylcarbinol] is oxidised by bromine and potassium hydroxide in aqueous solution to β -hydroxyisovaleric acid. With mesityl oxide, the oxidation results in the formation of $\beta\beta$ -dimethylacrylic acid. G. Y.

Action of Phosphorous Acid on Mannitol. Mannide. P. CARRÉ (*Compt. rend.*, 1903, 137, 517—520. Compare Abstr., 1903, i, 307 and 456, and Portes and Prunier, Abstr., 1902, i, 526).—When mannitol is heated with phosphorous acid at 125—130° under 18 mm. pressure, there is formed after one hour the ester, $C_4H_4(OH)_4[CH_2 \cdot O \cdot P(OH)_2]_2$, the crystalline *calcium* salt of which was isolated. When the heating is continued for 3—4 hours, there is also produced, probably by interaction of the foregoing ester with excess of mannitol, a *monophosphorous ester* of mannide, $C_6H_5O_3 \cdot O \cdot P(OH)_2$. Both these esters are monoacidic to helianthin and phenolphthalein, and are slowly hydrolysed by cold water.

Mannide readily reacts with phosphorus oxychloride at 50—60°, but is less readily esterified by phosphorous acid than mannitol, whence the author believes that Fauconnier's representation of mannide (Abstr., 1884, 1111) as a diprimary alcohol is inaccurate, the hydroxyls probably being present in secondary alcohol groups. The rates of esterification of mannitol and of mannide by phosphorous acid are tabulated in the original.

T. A. H.

Hydrolysis of Substances containing Pentosans by Dilute Acids or by Sulphites. Isolation of Pentoses. RUDOLF HAUERS and BERNHARD TOLLENS (*Ber.*, 1903, 36, 3306—3322).—Few systematic investigations on the hydrolytic decomposition of naturally-occurring products, containing pentosans and yielding pentoses on hydrolysis, have been made and the authors have accordingly studied the hydrolysis of cherry-gum by hydrochloric and by sulphuric acids of varying concentrations. Figures are quoted to indicate how the rate of the hydrolysis varies with the strength of the acid used and with the time during which the various solutions are boiled. Hydrochloric acid acts more quickly than sulphuric acid of an equivalent strength, and this difference between the two acids is also shown in the difference of the reducing power of the products of hydrolysis. For the preparation of arabinose from cherry-gum, sulphuric acid is more convenient than hydrochloric acid, since it can be separated so easily by means of calcium carbonate.

A specimen of gum from La Plata, which contained much pentosan and little galactan, was hydrolysed with sulphuric acid. It yielded magnesium lactate, arabinose (identified by the formation of the phenylbenzylhydrazone and the bromophenylhydrazone), and xylose (identified by the phenylbenzylhydrazone). Whilst cherry-gum contains much araban and very little xylan, the gum from La Plata, on the other hand, contains about equal quantities of those two pentosans, together with very little galactan. A specimen of an East African gum, which contained 22·58 per cent. of galactan, gave arabinose on hydrolysis, but neither xylose nor galactose was isolated. A specimen of myrrh-gum yielded both arabinose and xylose; this gum contained much xylan and less araban.

The method of hydrolysing gums by calcium sulphite is generally not so convenient as that by the mineral acids. Cherry-gum yielded arabinose but no xylose, whilst arabinose was also obtained from beet. Straw was found to contain much xylan and a little araban. Beech-

wood yielded xylose, but pine-wood gave very little arabinose and no xylose. When beet was hydrolysed by calcium sulphite, an acid having the composition $C_5H_{10}O_6$ was formed. When calcium sulphite is used, it is convenient to conduct the hydrolysis of the various substances containing pentosans at temperatures varying from 115° to 135° .

A. McK.

Hydrolysis of Starch by Acids. GEORGE W. ROLFE and H. W. GEROMANOS (*J. Amer. Chem. Soc.*, 1903, 25, 1003—1014).—It has been shown by Rolfe and Defren (Abstr., 1898, i, 7,) that in the products of the hydrolysis of starch by acids, a constant relation exists between the rotatory and cupric reducing powers. Brown, Morris, and Millar (*Trans.*, 1897, 71, 115) have confirmed this observation, and have shown that a similar relation also exists in the fractions obtained by precipitating the hydrolysed product with alcohol.

In the present paper, a table is given containing the recalculated values of Rolfe and Defren's work, together with the results of an additional series of determinations. On plotting these figures, it is found that the reducing values do not lie on a straight line as they should if dextrose only were present. The results are, however, in substantial agreement with the original results of Rolfe and Defren, and prove that the products of the acid hydrolysis of starch contain another reducing substance in addition to dextrose.

E. G.

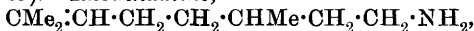
Presence of Maltose in Acid-hydrolysed Starch Products. GEORGE W. ROLFE and ISAAC T. HADDOCK (*J. Amer. Chem. Soc.*, 1903, 25, 1015—1019).—It has been stated by Morris, Rolfe and Defren, and others that maltose is one of the products of the hydrolysis of starch by acids. A 15 per cent. solution of a specimen of commercial glucose, which had been obtained by hydrolysis with hydrochloric acid under a pressure of 2 atmospheres, was added drop by drop to 10 times its volume of 95 per cent. alcohol. As a result of this fractional precipitation, a product was obtained which, when treated with phenylhydrazine, yielded maltosazone identical in crystalline character and other properties with that obtained from pure maltose.

E. G.

Transformation of Starch Paste. LÉON MAQUENNE (*Compt. rend.*, 1903, 137, 797—799. Compare Abstr., 1903, i, 679).—The author has examined the influence of temperature and of small quantities of mineral acids on the transformation of starch paste into amylocellulose, and finds (1) that the lower the temperature the more rapid and complete is the change, (2) the transformation is favoured by the presence of mineral acids (hydrochloric or sulphuric) even in quantities of $\frac{1}{10000}$, (3) the conversion tends towards a limit which at 0° and in a neutral medium appears to be at about 30 per cent.

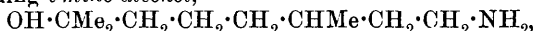
M. A. W.

Rhodinamine. LOUIS BOUVEAULT (*Bull. Soc. chim.*, 1903, [iii], 29, 1046—1049).—*Rhodinamine*,



obtained by reducing geranonitrile (Abstr., 1894, 83, and 1897,

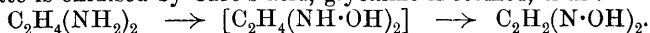
537) with metallic sodium in presence of alcohol, is a colourless liquid with an odour simultaneously recalling that of fish and that of roses. It boils at 105° under 15 mm. pressure, and has a sp. gr. 0.839 at $0^{\circ}/4^{\circ}$. The *salts* have a soapy appearance and are soluble in water, but are precipitated from their aqueous solutions by acids. Ethyl oxalate converts rhodinamine into a symmetrical disubstituted *oxamide*, which is crystalline and melts at 96° . When the amine, dissolved in moist ether, is treated with solid potassium hydroxide, it is converted into the corresponding *amino-alcohol*,



by the assumption of a molecule of water. This is a viscid liquid, which boils at 140° under 15 mm. pressure and has a sp. gr. 0.910 at $0^{\circ}/4^{\circ}$. The formation of rhodinamine affords no evidence as to whether the second ethylenic linking of geranionitrile occupies the $\alpha\beta$ - or $\beta\gamma$ -position.

T. A. H.

Oxidation of Ethylenediamine. EUGEN BAMBERGER and RICHARD SELIGMAN (*Ber.*, 1903, 36, 3831—3833).—When ethylenediamine hydrate is oxidised by Caro's acid, glyoxime is formed, thus:



The glyoxime was identified by its melting point, analysis, and the formation of hydroxylamine from it. The aqueous solution, from which the glyoxime had been removed, gave the ferric chloride reaction typical of hydroxamic acids.

A. McK.

Action of Methylamine and Dimethylamine on Mesityl Oxide. ARMIN HOCHSTETTER and MORITZ KOHN (*Monatsh.*, 1903, 24, 773—782. Compare Götschmann, *Annalen*, 1879, 197, 27, 38; Sokoloff and Latschinoff, *Ber.*, 1874, 7, 1387).—Methylamine and mesityl oxide form, almost quantitatively, an additive compound, which is probably methyldiacetonamine, $\text{NHMe}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{COMe}$, and not a compound of the constitution $\text{CHMe}_2\cdot\text{CH}(\text{NHMe})\cdot\text{COMe}$. Similarly dimethylamine and mesityl oxide form, less easily (40 per cent. unchanged mesityl oxide), an additive compound which is considered to be dimethyldiacetonamine, $\text{NMe}_2\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{COMe}$.

Methyldiacetonamine, which was not isolated, decomposes on distillation into mesityl oxide and methylamine; the *platinichloride*, $(\text{C}_7\text{H}_{15}\text{ON})_2\cdot\text{H}_2\text{PtCl}_6$, forms large, orange-red crystals. The *oxime* crystallises from light petroleum, melts at 57 — 59° , distils at 131° under 10 mm. pressure, and forms a *benzoyl* derivative which melts at 100 — 103° and an *oxalate*, $(\text{C}_7\text{H}_{16}\text{ON})_2\cdot\text{C}_2\text{H}_2\text{O}_4$, which crystallises from alcohol as a white powder.

Dimethyldiacetonamine, when heated, decomposes into dimethylamine and mesityl oxide. The *oxime* crystallises in white needles, sinters at 38 — 40° , and melts at 46 — 47° , boils at 136 — 138° under 17 mm. pressure, and forms an unstable *additive* compound with methyl iodide, and an *oxalate*, $(\text{C}_8\text{H}_{17}\text{ON})_2\cdot\text{C}_2\text{H}_2\text{O}_4$, which separates from alcohol as a white, hygroscopic powder.

G. Y.

isoGlucosamine. LÉON MAQUENNE (*Compt. rend.*, 1903, 137, 658—660).—The glucamine series of bases, prepared by the author and

Roux (Abstr., 1901, i, 372; 1903, i, 73, 436) by the reduction of the aldosoxyimes by sodium amalgam, bear the same relation to the glucosamines as exists between the polyhydric alcohols and the reduced sugars, the one passing into the other by the addition of hydrogen. Thus, when *isoglucosamine* is reduced by means of sodium amalgam in an alkaline solution, two stereoisomeric bases belonging to the glucamine series are produced, *d*-mannamine (identified by means of its oxalate melting at 186° with the salt prepared expressly for the purpose by Roux, by the reduction of mannosoxime), and *d*-glucamine. This fact confirms the presence of a ketonic grouping in *isoglucosamine*, and furnishes a means of passing from the mannitol to the sorbitol series and conversely.

M. A. W.

Ethyl β -Diethylaminopropionate. BERNHARD FLÜRSCHHEIM (*J. pr. Chem.*, 1903, [ii], 68, 345—356).—Ethyl β -iodopropionate is best prepared by heating β -iodopropionic acid with alcohol and sulphuric acid (Otto, Abstr., 1888, 360). If hydrochloric acid is used (Harries and Loth, Abstr., 1896, i, 321), part of the iodine is replaced by chlorine.

Ethyl β -diethylaminopropionate, formed by the action of an excess of diethylamine on ethyl β -iodopropionate, is a colourless liquid, which boils at 192° under 753 mm., and at 83—84° under 12 mm. pressure, and has a characteristic amine odour. It is moderately soluble in water, and easily in dilute hydrochloric acid, from its solution, in which it is quantitatively recovered by addition of sodium carbonate and extraction with ether. It is easily hydrolysed by dilute hydrochloric acid, even at the ordinary temperature. Addition of mercuric chloride to the aqueous solution of the ester produces a voluminous yellow precipitate, which quickly becomes scarlet, and is dissolved by sulphuric acid. The *hydrochloride* is very hygroscopic.

Diethylamine hydriodide, formed along with ethyl β -diethylaminopropionate, crystallises in colourless needles, melts at 168—170°, is not deliquescent, and dissolves easily in water or alcohol, but is only slightly soluble in benzene or ether. The action of ethyl β -diethylaminopropionate on ethyl β -iodopropionate in ethereal solution leads to the formation of ethyl acrylate, diethylamine hydriodide, and the *hydriodide* of ethyl β -diethylaminopropionate, which deliquesces on exposure to the atmosphere, and at 165° decomposes with formation of ethyl acrylate. Ethyl β -diethylaminopropionate is formed when ethyl acrylate is boiled with an excess of diethylamine.

β -Diethylaminopropionic acid, obtained from the ester by hydrolysis with dilute hydrochloric acid, is colourless, melts at 70—71°, is very hygroscopic, is easily soluble in water or alcohol, and insoluble in ether, has an acid reaction in aqueous solution, and is not decomposed by boiling aqueous sodium hydroxide. At 160°, the acid decomposes with formation of *diethylamine acrylate*, which evolves diethylamine when warmed with aqueous sodium hydroxide. On distillation of the diethylamine acrylate, there remains a colourless residue which is soluble in aqueous alkalis and is probably a polymerisation product of acrylic acid. *Ethyl sodio- β -diethylaminopropionate* is formed by the action of granulated sodium on the ester in ethereal solution; it is

decomposed by the action of water, glacial acetic acid, or hydrogen chloride, the chief products being unchanged ester and diethylamine. The action of benzyl chloride on the sodio-compound leads to the formation of benzyldiethylamine hydrochloride. From the products of the reaction between benzoyl chloride and the sodio-compound, there have been separated, unchanged ester, diethylamine, diethylbenzamide, ethyl benzoate, benzoic anhydride, a solid, brown substance which is soluble in alcohol or aqueous hydrochloric acid, and a basic oil which yields a yellow *platinichloride*.

Tetraethyltrimethylenediamine, formed by the action of trimethylene dibromide on diethylamine in toluene solution, is a colourless oil, which boils at 205—209°, has a characteristic odour, and, with mercuric chloride in aqueous solution, gives a colourless precipitate which rapidly becomes yellow and, finally, olive-green. The *mercurichloride*, $C_8H_{16}(NEt_2)_3 \cdot 2HCl \cdot 2HgCl_2$, crystallises in colourless, monoclinic prisms and melts at 124—125°.

Tetraethyltrimethylenediamine does not react with potassium, sodium, or benzoyl chloride. G. Y.

Action of Hydrogen Cyanide on Aldehyde-ammonia and Analogous Compounds. MARCEL DELÉPINE (*Compt. rend.*, 1903, 137, 984—986).—The equations generally assumed for the synthesis of amino-acids from aldehyde-ammonias and hydrogen cyanide cannot be applied to the reactions between hydrogen cyanide and ethylideneimine or methylmethyleamine. The hydrogen cyanide is added to the molecule at the double linking, as in the equations $CHMe:NH + HCN = CN \cdot CHMe \cdot NH_2$ and $CHMe:NR + HCN = CN \cdot CHMe \cdot NHR$. In many cases, the reaction is complicated by the polymerisation of the amino-nitriles first formed. C. H. D.

Action of Potassium Thiocyanate on Ammonium Heptamolybdate. I. C. REICHARD (*Chem. Zeit.*, 1903, 27, 1134—1135).—When potassium thiocyanate and a little hydrochloric acid are added to a solution of molybdic acid, an intense yellow coloration is produced, which disappears on the addition of ammonia or of potassium hydroxide solution, and is regenerated when the colourless solution is acidified. When a strong solution of potassium thiocyanate is added to a very dilute solution of ammonium molybdate, the solution, after 24 hours, deposits a white precipitate. When strong solutions of potassium thiocyanate and ammonium molybdate are mixed, the separation of this white compound takes place immediately. Alkaline tungstate solutions do not form a precipitate with potassium thiocyanate. By the action of potassium thiocyanate on ammonium molybdate, two distinct compounds of molybdenum and thiocyanic acid are formed. A. MCK.

Iodocyanides of Potassium and Cæsium. C. H. MATHEWSON and HORACE L. WELLS (*Amer. Chem. J.*, 1903, 30, 430—432).—By dissolving iodine in a concentrated solution of potassium cyanide, Langlois (*Ann. Chim. Phys.*, 1860, [iii], 60, 220) obtained a compound to which he assigned the formula $KI_4CNi_4H_2O$. It is now found that this salt contains only $1H_2O$. No evidence was obtained of the

existence of any other compound of the iodides of potassium and cyanogen.

Cæsium iodocyanide, $\text{CsI} \cdot 2\text{CNI}$, forms cinnamon-coloured, orthorhombic plates, and is sparingly soluble in water. This is the only double salt of cæsium and cyanogen iodides which could be obtained.
E. G.

Compound of Mercuric Cyanide and Cæsium Iodide. C. H. MATHEWSON and HORACE L. WELLS (*Amer. Chem. J.*, 1903, 30, 432—433).—Mercuric cyanide combines with cæsium iodide in only one proportion forming the compound, $\text{CsI} \cdot \text{Hg}(\text{CN})_2$, which crystallises in white, pearly plates, and is decomposed by acids with formation of hydrogen cyanide and mercuric iodide. It can be recrystallised readily from water, and remains unchanged in composition.
E. G.

Chemical Equilibrium Between Hydroferrocyanic and Hydroferricyanic Acids. MAURICE PRUD'HOMME (*Bull. Soc. chim.*, 1903, [iii], 29, 1009—1010).—The author finds that solutions of hydroferricyanic acid give a blue coloration with filter papers impregnated with guaiacum tincture, and that consequently this indicator cannot be used to determine the end-point in the titration of ferrocyanides with chromic acid solutions. This change is a reversible one, and the titration liquid acquires the property of giving a blue colour with guaiacum at the equilibrium point. If the titration is continued beyond this point until the liquid no longer gives a blue colour with filter paper (due to the latter containing traces of chlorine introduced in bleaching the pulp), then the conversion of hydroferrocyanic into hydroferricyanic acid is complete. Measurement of the volumes of chromic acid solutions requisite to produce (a) equilibrium and (b) complete conversion, indicate that the relative velocities of the oxidising and deoxidising reactions are as 10 : 1. A process is given for estimating soluble ferrocyanides by titration with chromic acid, based on these observations.
T. A. H.

Chemical Equilibrium between Potassium Ferrocyanide and Ferricyanide in presence of Alkali Hydroxides. MAURICE PRUD'HOMME (*Bull. Soc. chim.*, 1903, [iii], 29, 1010—1012).—Potassium ferricyanide is converted into potassium ferrocyanide by prolonged ebullition of its aqueous solutions in presence of alkali hydroxides, but the reduction is complete only in presence of reducing agents, for instance, dextrose and indigotin. The rapidity of oxidation of indigotin by ebullition with solutions containing sodium hydroxide and potassium ferricyanide is directly proportional to the concentration of these two substances in the solutions, but in presence of these and of potassium ferrocyanide the rate becomes inversely proportional to the concentration of the ferrocyanide.

It is suggested that when solutions containing potassium ferricyanide and hydroxide are boiled, equilibrium is reached in the reversible reaction $\text{K}_6\text{Fe}_2\text{Cy}_{12} + 2\text{KOH} \rightleftharpoons 2\text{K}_4\text{FeCy}_6 + \text{H}_2\text{O}_2$. In conformity with this view it was observed that (a) potassium ferricyanide and hydroxide are formed when a solution of hydrogen peroxide is added to one of

potassium ferrocyanide, (b) the addition of excess of hydrogen peroxide to a solution containing potassium ferricyanide and sodium hydroxide results eventually in the formation of potassium ferrocyanide and the evolution of oxygen, and (c) the bleaching of indigotin by hydrogen peroxide is much more rapid in presence of an alkali hydroxide than in acid solution.

T. A. H.

Systematic Alkylation of Arsenic. VICTOR AUGER (*Compt. rend.*, 1903, 137, 925—927).—By an extension of Meyer's method of methylating sodium arsenite (Abstr., 1883, 1078), the author has obtained arsenious compounds containing one, two, or three methyl groups. Sodium monomethylarsonate, $\text{AsMeO}(\text{ONa})_2$, is reduced by sulphur dioxide to methylarsenoxide, AsMeO , which, in the form of its disodium derivative, $\text{AsMe}(\text{ONa})_2$, reacts readily with methyl iodide to give the sodium derivative of cacodylic acid, $\text{AsMe}_2\text{O}\cdot\text{ONa}$; the reduction of this compound yields cacodyl oxide, the sodium derivative of which, $\text{AsMe}_2\cdot\text{ONa}$, reacts with methyl iodide to form the oxide of trimethylarsine, AsMe_3O .

Attempts to prepare the corresponding ethyl derivatives have been less successful, and not yet carried beyond the stage of ethylarsonic acid, $\text{AsEtO}(\text{OH})_2$.

M. A. W.

Inorganic Additive Compounds of Unsaturated Substances. JULIUS SAND (*Annalen*, 1903, 329, 135—166).—The compounds of mercury salts with ethylene and its derivatives, the compounds of cobaltous ammonium salts with oxygen, and the compounds of cobaltic ammonium salts with nitric oxide are discussed in this paper.

A summary of the chief compounds obtained from mercury salts and ethylene derivatives is given, the substances prepared from unsaturated alcohols and oximes being considered in detail; it is pointed out that only the simple ethylene linking is capable of forming an additive compound with mercury salts, whilst a conjugated pair of ethylene linkings, which will take up bromine, and the ethylene linkings in benzene, which will not combine with bromine, are neither of them able to combine with mercury salts.

Attention is drawn to the fact that these organo-mercury compounds behave very differently towards different acids, &c.; thus they are immediately decomposed by hydrochloric and hydrobromic acids and by potassium cyanide, an ethylene linking being regenerated; for example, mercurylethanol bromide yields ethylene. Nitric and sulphuric acids are without action on these substances. It would appear that mercury compounds of this type can only be decomposed by reagents which will form complex negative ions with the mercury, as, for example, (HgCl_4) , or (HgSCN_4) . It is suggested that in these complex mercury ions the mercury atom is quadrivalent, but that two of the valencies are of a different order from the others. Further, it is possible that two series of mercurylethanol salts exist; in one, the metal is quadrivalent, and is linked with the partial valencies of the ethylene, whilst in the other the linkage is represented by the formula $\text{IHg}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$; acids and other compounds which are capable of forming a complex ion with the mercury bring about the

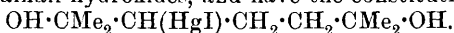
conversion of the latter compound into that first mentioned,

$$\begin{array}{c} \text{CH}_2 \cdots \\ | \\ \text{CH}_2 \cdots \end{array} \text{Hg} \begin{array}{c} \diagup \text{I} \\ \diagdown \text{OH} \end{array}$$

The addition of oxygen and nitric oxide to cobaltamines is discussed at considerable length; the author sees in both phenomena the exhibition of "partial" or subsidiary valency in the molecule of oxygen and nitric oxide.

K. J. P. O.

Action of Mercuric Salts on Unsaturated Alcohols and Oximes. JULIUS SAND and FRITZ SINGER (*Annalen*, 1903, 329, 166—194. Compare Abstr., 1902, i, 851 and preceding abstract).—Dimethylheptenol, prepared from methylheptenol (*loc. cit.*), readily reacts with aqueous mercury acetate, forming a solution from which alkaline potassium iodide precipitates two pairs of isomeric iodides. One pair of *iodides* are soluble in alkali hydroxides, and have the constitution

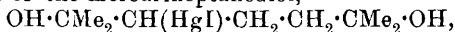


The α -form is a solid melting at 124—125°, and differs from the β -form in solubility and stability towards acids. The other pair of *iodides* are

cyclic compounds, $\text{HgI} \cdot \text{CH} \begin{array}{c} \text{CMe}_2 \text{---O} \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{CMe}_2$, and are prepared by

shaking the heptenol with aqueous mercury acetate, adding 10 per cent. potassium hydroxide to the clear solution, and then introducing aqueous potassium iodide; the β -iodide of mercuridimethylheptene oxide separates as an oil, extremely soluble in alcohol, but only slowly acted on by alkalis. The α -iodide is prepared in the same manner as the β -compound, and separates as a solid containing the β -form, which is extracted by treatment with cold alcohol; the pure substance forms white crystals melting at 108—110°, and is the stable form as the β -form slowly changes into it in the presence of alkali, the reverse transformation never taking place.

The β -iodide of the mercuriheptenediol,



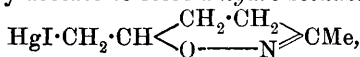
is precipitated in the form of an oil by carbon dioxide from the alkaline liquor from which the insoluble cyclic iodides have separated. It is transformed into the stable α -modification either when its benzene solution is boiled or by keeping its alkaline solution for several weeks; the α -iodide forms well-developed crystals melting and decomposing at 124—125°, and is less soluble in benzene or alkali than the β -modification.

Ethylhexenol, $\text{CH}_2 \cdot \text{CH} \cdot [\text{CH}_2]_2 \cdot \text{CMeEt} \cdot \text{OH}$, is prepared by the action of ethyl bromide on allylacetone in the presence of magnesium powder and is a liquid boiling at 65° under 14 mm. pressure; it dissolves readily in aqueous mercuric acetate; from the solution, alkaline potassium iodide precipitates an oil, the separation of which is completed by passing in carbon dioxide; after treatment with ether, a crystalline substance is obtained melting at 44°, and is probably a tetra-

hydrofurfuran derivative, $\begin{array}{c} \text{CH}_2 \text{---} \text{CMeEt} \\ | \\ \text{CH}_2 \cdot \text{CH}(\text{CH}_2 \cdot \text{HgI}) \end{array} \text{O}$, since under the action of iodine, an oily iodide is formed, which is shown by treatment with permanganate to be saturated; when it is oxidised by chromic

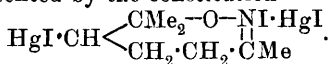
acid, an aldehyde is produced. Hydrochloric acid converts the original mercuri-iodide back into ethylhexenol.

Allylacetoxime (an oil boiling at 190° under 720 mm. pressure) reacts with mercury acetate to form a *hydroisooxazole* derivative,



which is purified by washing with ether and recrystallising from alcohol, when it melts at 122°.

Methylheptenoneoxime yields several hydrogenated *isooxazole* derivatives according as the reaction between the mercury salt and the oxime takes place in acid or alkaline solution. When the oxime is treated with mercury acetate in acid solution and the resulting product precipitated with potassium iodide, a mixture of two *substances* is obtained, which can be separated by treatment with cold alcohol, in which the one is soluble, whilst the other is not; the soluble substance, the α -modification, forms white crystals melting at 94°, the other is a yellow, crystalline solid and melts at 123°; they are probably both represented by the constitution



The substance melting at 94° yields a *picrate* (probably an oxonium picrate), $(\text{C}_8\text{H}_{14}\text{ONHg}_2\text{I}_3)_2 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$, which is crystalline, sinters at 65° and melts at 78–80°. When potassium bromide is substituted for potassium iodide in the preparation of the *isooxazole* derivative, a *bromide*, $\text{C}_8\text{H}_{14}\text{ONBr}_3\text{Hg}_2$, is obtained as white crystals melting at 123°; both the iodides and the bromide are soluble in alkali hydroxides without precipitation of mercury oxide, and under the influence of hydrazine, in the presence of alkali, lose half their mercury, which is precipitated as metal.

When the interaction of the ethylhexenol and mercury acetate takes place in the presence of potassium hydrogen carbonate, an oil separates on addition of potassium iodide, and is converted into a crystalline solid on repeated solution in methyl alcohol and precipitation with ether; this substance, $(\text{C}_8\text{H}_{14}\text{ONIHg})_2 \cdot \text{HgI}_2$, melts and decomposes at 150°; in the mother liquors, a more soluble isomeride, the α -form, is found, and can be obtained as a crystalline powder melting at 114°.

Mercuryethanol bromide can be converted by evaporation with acetic anhydride into an *acetyl* derivative, $\text{HgBr} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OAc}$, which crystallises in lustrous leaflets melting at 75°. When treated with hydrochloric acid, ethylene is evolved. When oxidised by permanganate, the ethanol bromide is mainly converted into oxalic acid, the *bromide* of mercuriacetic acid, $\text{HgBr} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, being at the same time produced; it crystallises in colourless needles melting at 198°, and is not decomposed by hydrochloric acid. K. J. P. O.

Mercury Compounds of Ketones. JULIUS SAND and OTTO GENSSLER (*Ber.*, 1903, 36, 3699–3706).—When mercuric acetate is heated with acetone under pressure at 100°, a crystalline compound, $\text{C}_6\text{H}_{10}\text{O}_3\text{Hg}_4(\text{C}_2\text{H}_3\text{O}_2)_4$, is formed, which can be recrystallised from

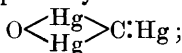
alcohol to which a drop of acetic acid has been added ; it melts at 157° and probably has the following constitution:

$\text{CH}(\text{Hg}\cdot\text{OAc})_2\cdot\text{CMe}(\text{OH})\cdot\text{O}\cdot\text{CMe}(\text{OH})\cdot\text{CH}(\text{Hg}\cdot\text{OAc})_2$;
potassium hydroxide converts this acetate into an insoluble *oxide*, $\text{C}_6\text{H}_{10}\text{O}_5\text{Hg}_4$.

Methyl ethyl ketone forms a similar oxonium compound with mercuric acetate, which combines with $\frac{1}{2}$ mol. of picric acid.

Dihydronaphthalene forms with mercuric acetate an *acetate*, crystallising either from benzene or light petroleum in long needles melting at 122° . This is soluble in potassium hydroxide ; potassium bromide precipitates the corresponding *bromide*, which crystallises from benzene in white, glistening needles melting at 159° . The *iodide* is also insoluble in alkali ; it melts at 156° . E. F. A.

Mercuric Acetate and Acetic Anhydride. JULIUS SAND and FRITZ SINGER (*Ber.*, 1903, 36, 3707—3710).—On heating mercuric acetate with freshly distilled acetic anhydride at the temperature of the water-bath, it gradually goes into solution, forming a complicated mercury derivative of acetic acid, $\text{O}\langle\text{Hg}\rangle\text{C}(\text{Hg}\cdot\text{OAc})_2$. This *acetate* is insoluble in organic solvents, dissolves and decomposes in hydrogen chloride solutions, but is soluble in cold 20 per cent. nitric acid ; on precipitation with much water, a *nitroacetate*, $\text{OAc}\cdot\text{Hg}\rangle\text{C}\langle\text{Hg}\rangle\text{O}$, is formed. Both these compounds are non-explosive, but the free base, prepared by decomposing the diacetate with cold potassium hydroxide is an exceedingly explosive compound. It is colourless, easily soluble in cold 20 per cent. hydrochloric acid or in potassium cyanide solution, and has the constitution $\text{O}\langle\text{Hg}\rangle\text{C}\langle\text{Hg}\rangle\text{O}$, $2\frac{1}{2}\text{H}_2\text{O}$. When heated at 160° , it loses carbon dioxide and water, forming probably a methane derivative,



reduction with sodium amalgam converts it into silver acetate, whilst potassium iodide forms the corresponding iodide. E. F. A.

New Synthesis of Hydrocarbons by means of Organo-magnesium Compounds. ALFRED WERNER (*Ber.*, 1903, 36, 3618—3619).—A question of priority (see Houben, *Abstr.*, 1903, i, 805, and Werner and Zilkens, *ibid.*, 615). C. H. D.

Hydrides of Cyclic Hydrocarbons. JOHANN F. EIJKMAN (*Chem. Centr.*, 1903, ii, 989 ; from *Chem. Weekblad.*, 1, 7—12).—The following cyclic hydrocarbons have been prepared by Sabatier and Senderens' method of forming hydro-compounds in presence of nickel.

Tricyclodecane, $\text{CH}_2\langle\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\rangle\text{CH}_2$, obtained from *dicyclopentadiene*, crystallises from alcohol or glacial acetic acid, melts at 77° ,

boils at 86° under 24 mm., at 123° under 100 mm., or at 193° under 769 mm. pressure, and has a sp. gr. 0.9120 at 80° ; it has a taste and odour similar to those of camphor, and is not attacked by concentrated sulphuric acid, but by prolonged heating with concentrated sulphuric acid and a small quantity of pyrosulphuric acid at a temperature a little above the melting point, it forms an isomeride which melts at about 9° , boils at 191.5° under 769 mm. pressure, and has a sp. gr. 0.9021 at 80° . These substances are probably *cis*- and *trans*-stereoisomerides. Cyclopentane, C_5H_{10} , prepared from cyclopentadiene, is liquid at -80° , boils at 49° under 760 mm. pressure, and has a sp. gr. 0.7517 at 12.7° .

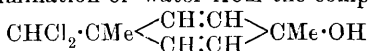
Hydrindene yields dicyclononane, $\begin{array}{c} CH_2 \cdot CH_2 \cdot \dot{C}H \cdot CH_2 \\ | \quad | \\ CH_2 \cdot CH_2 \cdot \dot{C}H \cdot CH_2 \end{array} > CH_2$, which boils at 163 — 164° and has a sp. gr. 0.8759 at 23° . Dicyclotridecane (dodecahydrodiphenylmethane), $C_6H_{11} \cdot CH_2 \cdot C_6H_{11}$, prepared from diphenylmethane, boils at 150° under 45 mm. or at 251.5° under 760 mm. pressure, and has a sp. gr. 0.8765 at 19.7° ; it crystallises from its solution in ether when cooled by means of alcohol and carbon dioxide. Diphenyl yields phenylcyclohexane, $C_6H_5 \cdot C_6H_{11}$, which melts at about 0° , boils at 106° under 12 mm., at 156° under 80 mm., or at 238° under 770 mm. pressure, and has a sp. gr. 0.9306 at 17.1° .

E. W. W.

Action of Nascent Acetylene on Benzene in presence of Aluminium Chloride. E. PARONE (*L'Orosi*, 1902, 25, 148—153).—The action of nascent acetylene on benzene in presence of aluminium chloride, when allowed to continue for several days, during which the aluminium chloride and calcium carbide were frequently renewed, was found to yield mainly ethylbenzene, styrene, dibenzyl, and anthracene. The formation of these compounds is explained by Friedel and Craft's theory of the action of aluminium chloride in organic syntheses.

T. H. P.

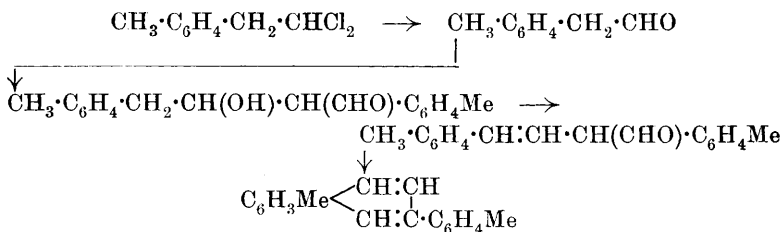
Cyclic Ketones from Chloroform and Phenols. KARL AUWERS and G. KEIL (*Ber.*, 1903, 36, 3902—3911).—The substance $C_9H_{10}Cl_2$, obtained by the elimination of water from the compound



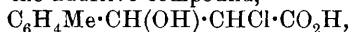
(*Abstr.*, 1903, i, 620), on oxidation with chromic acid in acetic acid solution gives $\beta\beta$ -dichloro-*p*-ethylbenzoic acid, and is therefore *p*-methyl- $\beta\beta$ -dichloroethylbenzene, $CH_3 \cdot C_6H_4 \cdot CH_2 \cdot CHCl_2$.

$\beta\beta$ -Dichloro-*p*-ethylbenzoic acid, $CHCl_2 \cdot CH_2 \cdot C_6H_4 \cdot CO_2H$, crystallises from benzene in slender, white needles, melts at 179 — 181° , and on reduction with sodium dissolved in alcohol gives *p*-ethylbenzoic acid.

The hydrocarbon, $C_{18}H_{16}$, obtained by the action of water at a high temperature on *p*-methyl- $\beta\beta$ -dichloroethylbenzene is shown to be 3-methyl-6-*p*-tolyl-naphthalene by the following considerations; its formation from *p*-methyl- $\beta\beta$ -dichloroethylbenzene may therefore be expressed as follows:



p-Methyl- β -chlorostyrene, $\text{C}_6\text{H}_4\text{Me} \cdot \text{CH} : \text{CHCl}$, prepared either by heating the chloride, $\text{C}_9\text{H}_{10}\text{Cl}_2$, with alcoholic potassium hydroxide, or synthetically by adding a solution of sodium carbonate saturated with chlorine to an alkaline solution of *p*-methylcinnamic acid and subsequently distilling the additive compound,



formed, with dilute sulphuric acid, crystallises from methyl alcohol in slender, white needles, melts at $36-37^\circ$, and boils at $128-134^\circ$ under $38-41$ mm. or at $222-224^\circ$ under the ordinary pressure. The analogous *p*-methyl- β -bromostyrene, $\text{C}_6\text{H}_4\text{Me} \cdot \text{CH} : \text{CHBr}$, crystallises from methyl alcohol in long prisms and melts at $46.5-47.5^\circ$. When either of the foregoing compounds is heated with water for 3 hours at $170-180^\circ$, the hydrocarbon, $\text{C}_{18}\text{H}_{16}$, is obtained.

β -Phenylacetaldehyde (compare Zincke and Breuer, Abstr., 1885, 269) is easily converted into β -phenylnaphthalene by heating it with dilute hydrochloric acid for 3 hours at $170-180^\circ$; the same substance is formed by similarly treating β -chlorostyrene. $\beta\beta$ -Dichloroethylbenzene, $\text{CH}_2\text{Ph} \cdot \text{CHCl}_2$, has been described by Forrer (Abstr., 1884, 1020) as decomposing spontaneously at the ordinary temperature, but the authors have prepared it by the action of phosphorus pentachloride on phenylacetaldehyde, and find that it boils at $110-119^\circ$ under 25 mm. or at $210-220^\circ$ under 760 mm. pressure without decomposition occurring; it has a sp. gr. 1.153 at 18° .

β -Phenylacetaldehydesemicarbazone crystallises from dilute alcohol in small, thick prisms and melts at 153° . W. A. D.

Amylbenzenes. AUGUST KLAGES (*Ber.*, 1903, 36, 3688-3694. Compare Abstr., 1903, i, 19).—*a*-Methylbutylbenzene [*sec*-Amylbenzene], $\text{CHMePh} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Me}$, is easily soluble in sulphuric acid containing 6 per cent. of sulphur trioxide, forming a *sulphonic acid* which yields crystalline *sodium* and *barium* ($+\text{H}_2\text{O}$) salts; the *sulphonic chloride* is a clear, viscous oil boiling at 194° under 12 mm. pressure and having a sp. gr. 1.1751 at $15^\circ/4^\circ$ and n_D 1.5308. The *amide* crystallises from light petroleum in glistening needles and melts at $66-67^\circ$, the *benzylamide* melts at $62-64^\circ$, and the *anilide* forms well-defined prisms melting at $60-61^\circ$.

Phenylmethylisopropylcarbinol, $\text{CMePr}^a\text{Ph} \cdot \text{OH}$, produced by the interaction of isobutyrylbenzene and magnesium methiodide in the cold, is a colourless, viscid oil boiling at $109-110^\circ$ under 12 mm. or at $196-198^\circ$ under atmospheric pressure, and having a sp. gr. 0.9653 at $13.5^\circ/4^\circ$ and n_D 1.51611. The corresponding *chloride* is a colourless

oil having an odour of cymene and losing hydrogen chloride when heated.

α -iso*Propylvinylbenzene* [β -phenyl- Δ^{α} -amylene], $\text{CH}_2\text{:CPrPh}$, obtained by heating the chloride with pyridine, is an oil boiling at 82° under 12 mm. or at $191\text{--}192^\circ$ under 753 mm. pressure, and having a sp. gr. 0.8991 at $13.8^\circ/4^\circ$ and n_D 1.5181; it forms an oily *dibromide*. When reduced with sodium and alcohol, it is converted into $\alpha\beta$ -*dimethylpropylbenzene* [sec.-isoamylbenzene], $\text{CHMePh}\cdot\text{CHMe}_2$, boiling at $188\text{--}189^\circ$ and having a sp. gr. 0.8672 at $16^\circ/4^\circ$ and n_D 1.4972; it dissolves in sulphuric acid, the *barium* salt of the *sulphonic acid* crystallising (with $2\text{H}_2\text{O}$) in glistening plates.

Phenyldiethylcarbinol is a colourless, viscid oil boiling at $107\text{--}109^\circ$ under 14 mm. or at $223\text{--}224^\circ$ under atmospheric pressure; it has a sp. gr. 0.9706 at $12.5^\circ/4^\circ$, and n_D 1.51665. The *chloride* is a colourless, odourless oil; it is converted on heating with pyridine into α -ethyl*propenyl benzene* [γ -phenyl- Δ^{β} -amylene], $\text{CEtPh}\cdot\text{CHMe}$, a colourless oil with a strong cymene-like odour, boiling at $91\text{--}93^\circ$ under 18 mm. or at $197\text{--}198^\circ$ under 753 mm. pressure, and having a sp. gr. 0.9173 at $14^\circ/4^\circ$ and n_D 1.5266. It unites with bromine and forms a *nitrosochloride* melting at 117° . On reduction, it forms α -ethylpropylbenzene [phenyldiethylmethane], CHEt_2Ph , which boils at $73\text{--}74^\circ$ under 12 mm. or at 187° under 753 mm. pressure, and has a sp. gr. 0.8755 and n_D 1.4988. The *sulphonic acid* forms a barium salt crystallising with H_2O and a *sulphonamide* crystallising from alcohol in glistening plates or needles melting at $89\text{--}90^\circ$. These constants are slightly different from those given by Dafert (Abstr., 1883, 659).

E. F. A.

Influence of Sulphur and of Sulphur-containing Groups on the Order of Substitution of Hydrogen Atoms in Cyclic Nuclei. Sulphur Derivatives of Phenyl Sulphide. EDOUARD BOURGEOIS and KARL PETERMANN (*Rec. trav. chim.*, 1903, 22, 349—355 and 356—366).—When phenyl sulphide is dissolved in sulphuric acid at 15° , a mixture of thiodibenzenedi-*o*-sulphonic acid and its *para*-isomeride is formed, whilst the latter only is produced when the solution is effected at 100° (compare Krafft, Abstr., 1875, 153, and Otto and Tröger, Abstr., 1893, 416). The two acids can be separated most readily by conversion into the corresponding chlorides and fractional crystallisation of the mixed chlorides from benzene.

Thiodibenzenedi-*p*-sulphonic acid, $\text{S}(\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H})_2$, crystallises in masses of tangled lamellæ and is very hygroscopic. The corresponding chloride, obtained by the action of phosphorus pentachloride on the potassium salt of the acid, crystallises from benzene in colourless prisms and melts at 159° (compare Otto and Tröger, *loc. cit.*); it is readily hydrolysed by methyl or ethyl alcohol, regenerating the acid and forming methyl or ethyl ether, but not by water. When dry methyl alcohol is treated with one third of its weight of the chloride at 15° , *methyl thiodibenzenedi-p-sulphonate* is formed; this crystallises in brilliant prisms and at first melts at 97° , but after preservation for some weeks the melting point rises to 118° and then

remains constant even after recrystallisation. The two forms of the methyl ester yield the original acid on hydrolysis.

Thiodibenzenedi-p-sulphonamide, $S(C_6H_4 \cdot SO_2 \cdot NH_2)_2$, prepared by the action of excess of ammonium carbonate on the chloride at 80° , forms colourless, crystalline crusts, melts at 195° , and is sparingly soluble in the usual solvents; the corresponding *sulphonanilide*, similarly prepared, crystallises from boiling alcohol in silky, prismatic needles and melts at 212.5° .

Thiodibenzenedi-p-sulphinic acid, $S(C_6H_4 \cdot SO_2H)_2$, prepared by reducing the disulphonic chloride, dissolved in benzene, with moist zinc dust, crystallises in brilliant leaflets, decomposes between 107° and 110° , and on reduction with zinc and hydrochloric acid furnishes the corresponding *di-p-thiol*, $S(C_6H_4 \cdot SH)_2$; this crystallises from alcohol in brilliant spangles, melts at 116.5° , and boils at $147.5-148.5^\circ$ under 11.5 mm. pressure: the *lead mercaptide* is an orange-yellow precipitate which decomposes at 278° , the *methyl thio-ether*, $S(C_6H_4 \cdot SMe)_2$, prepared by the interaction of methyl iodide with the sodium derivative of the dithiol, forms large, brilliant lamellæ and melts at 89° . When the lead mercaptide is treated with bromobenzene, no phenyl thio-ether is formed (compare Bourgeois, Abstr., 1896, i, 17). The non-reactivity of the lead derivatives of dithiols with the bromo-derivatives of cyclic hydrocarbons is due, it is suggested, to the inclusion of the lead atom in a cyclic structure, thus: $S \begin{smallmatrix} \text{C}_6\text{H}_4 \cdot \text{S} \\ \text{C}_6\text{H}_4 \cdot \text{S} \end{smallmatrix} \text{Pb}$.

Sulphonedibenzenedi-p-sulphonic chloride, $SO_2(C_6H_4 \cdot SO_2Cl)_2$, obtained by oxidation of the disulphonic chloride, dissolved in acetic acid, with potassium permanganate, crystallises from acetic acid in minute crystals, melts and decomposes at $217-220^\circ$, and is sparingly soluble in the usual solvents; when heated at 210° with phosphorus pentachloride it is converted into *p*-dichlorobenzene and thionyl chloride. The isomeride obtained by Otto and Rössing (Abstr., 1887, 263), which melts at $175-176^\circ$ and is readily soluble in benzene, is probably the *meta*-compound.

Thiodibenzenedi-o-sulphonic chloride crystallises from ether or acetic acid in minute prisms and melts at $95-96^\circ$ (the melting point is also given as $94-95^\circ$ in the first paper). When oxidised by potassium permanganate, it is converted into the corresponding *sulphone*; this crystallises from benzene in minute prisms (perhaps containing benzene of crystallisation), melts at $80-90^\circ$, at the same time giving off benzene, then solidifies and re-melts at $147-148^\circ$. On exposure to air, the prismatic crystals become opaque and finally disintegrate. When heated at 210° with phosphorus pentachloride, it is converted first into *o*-chlorobenzenesulphonic chloride and *o*-benzenedisulphonic chloride and eventually into *o*-dichlorobenzene and thionyl chloride.

T. A. H.

Aromatic Disulphinic Acids. JULIUS TRÜGER and WILHELM MEINE (*J. pr. Chem.*, 1903, [ii], 68, 313-340. Compare Otto and Casanova, Abstr., 1888, 255; Autenrieth and Hennings, Abstr., 1902, i, 390).—The aromatic disulphinic acids are more easily soluble in

water, less soluble in ether, and have less tendency to crystallise than the monosulphinic acids.

Zinc benzene-*m*-disulphinate, $C_6H_4(SO_2)_2Zn \cdot 3H_2O$, formed by the action of zinc dust on *m*-benzenedisulphonic chloride, crystallises from water (Pauly, *Ber.*, 1876, 9, 1595).

Whilst the action of chlorine or bromine on potassium benzene-*m*-disulphinate in aqueous solution leads to the formation of benzene-*m*-disulphonic chloride and bromide respectively, the action of iodine in aqueous potassium iodide or alcoholic solution results in oxidation of the disulphinate to benzene-*m*-disulphonic acid.

Benzene-*m*-disulphonic bromide, $C_6H_4(SO_2Br)_2$, separates from ether in yellow crystals and melts at 52° (compare Abstr., 1891, 718; 1893, i, 276).

When heated with water at 150° , benzene-*m*-disulphinic acid yields benzene-*m*-disulphonic acid (Abstr., 1902, i, 599) and *phenylenebenzene-m-dithiosulphonate*, $C_6H_4(SO_2 \cdot S)_2 \cdot C_6H_4$, which is a white, amorphous powder, insoluble in water. *Methyl benzene-m-disulphinate*, formed by the action of methyl chlorocarbonate on the potassium salt, is a viscid, yellow oil.

m-Phenylenebisalkylsulphones are obtained by the action of the alkyl haloid on potassium benzene-*m*-disulphinate.

m-Phenylenebismethylsulphone, $C_6H_4(SO_2Me)_2$, crystallises in white leaflets and melts at $195-196^\circ$. *m*-Phenylenebispropylsulphone crystallises in white needles and melts at $109-110^\circ$. *m*-Phenylenebis-*n*-butylsulphone is a yellow oil, is easily soluble in alcohol or ether, and insoluble in water. *m*-Phenylenebisallylsulphone crystallises in white leaflets and melts at 105° . *m*-Phenylenebisdichloropropylsulphone, $C_6H_4(SO_2 \cdot C_3H_5Cl_2)_2$, formed by the action of chlorine on the diallylsulphone in chloroform solution, is a yellowish-brown, viscid mass. *m*-Phenylenebisdibromopropylsulphone is a yellow, viscid oil. *m*-Phenylenebisbromopropylsulphone, $C_6H_4(SO_2 \cdot C_3H_5Br)_2$, crystallises in white leaflets and melts at 74° . *m*-Phenylenebisiodomethylsulphone is formed when methylene iodide and potassium benzene-*m*-disulphinate are heated together under atmospheric pressure, and melts at 248° (compare Autenrieth and Hennings, *loc. cit.*).

m-Phenylenebisacetonylsulphone, formed by warming chloroacetone with potassium benzene-*m*-disulphinate in alcoholic solution, crystallises in slightly yellow needles, melts at $150-151^\circ$, and forms a dioxime, $C_6H_4(SO_2 \cdot CH_2 \cdot CMe : N \cdot OH)_2$, which crystallises in yellow, prismatic needles and melts at $198-199^\circ$. The action of phenylhydrazine on *m*-phenylenedi-acetonylsulphone leads to the formation of a *monophenyldiazone*, $C_6H_4(SO_2 \cdot CH_2 \cdot CMe) \cdot SO_2 \cdot CH_2 \cdot CMe : N_2HPh$, which crystallises in nodules and melts and decomposes at 152° , and a *diphenyldiazone*, which separates from alcohol in glistening, yellow crystals and melts and decomposes at 172° .

Methyl m-phenylenebis-sulphoneacetate, $C_6H_4(SO_2 \cdot CH_2 \cdot CO_2Me)_2$, formed by the action of methyl chloroacetate on potassium benzene-*m*-disulphinate, separates from ethyl acetate in thick, white crystals and melts at $96-97^\circ$. The *ethyl* ester, formed by the action of ethyl chloroacetate, crystallises in white leaflets, melts at $86-87^\circ$, and, on hydrolysis with aqueous sodium hydroxide, yields *m-phenylenebis-sul-*

phloneacetic acid, which crystallises in white needles, and, when heated, decomposes with formation of phenylenedi-methylsulphone (?).

m-Phenylenebis-sulphoneacetamide, formed by the action of chloroacetamide on potassium benzene-*m*-disulphinate, crystallises in white needles, melts at 229—230°, and at higher temperatures loses ammonia with formation of the *imide*. *Ethyl m-phenylenebis-sulphonepropionate* is a yellow oil and, on hydrolysis, yields the *acid*, $C_6H_4(SO_2 \cdot CH_2 \cdot CO_2H)_2$, which is a colourless oil; the *barium* salt forms white crystals. *Ethyl m-phenylenebis-sulphonebutyrate* crystallises in white needles and melts at 96°; the *acid* is an oil; the *barium* salt crystallises in stellate aggregates of needles.

Potassium *m*-phenylenedi-thiosulphonate (Abstr., 1902, i, 599) is formed when potassium *m*-phenylenedisulphinate and sulphur are heated together; it crystallises from alcohol in long, white needles.

Benzene-*p*-disulphinic acid, which crystallises in small, white needles, is formed by the action of sulphuric acid on a concentrated aqueous solution of *potassium benzene p-disulphinate*, prepared by Schiller and Otto's method (this Journal, 1877, i, 312), from benzene-*p*-disulphonic chloride. The *barium* salt, $C_6H_4(SO_2)_2Ba$, is white.

p-Phenylenebismethylsulphone, formed by the action of methyl iodide on potassium benzene-*p*-disulphinate, crystallises in flat, white needles and melts at 255—256°.

Zinc toluene-2:4-disulphinate, prepared by the action of zinc dust on toluene-2:4-disulphonic chloride, crystallises in thin, white needles, and, with concentrated aqueous potassium carbonate solution, yields the *potassium* salt from which the acid is prepared. *Toluene-2:4-disulphinic acid*, $C_7H_6(SO_2H)_2$, is an oil, is soluble in water, and in presence of moisture bleaches litmus paper; the *sodium* salt and the *barium* salt form white crystals. When heated with water, toluene-2:4-disulphinic acid yields toluene-2:4-disulphonic acid and *tolylene toluene-2:4-di-thiosulphonate*, $C_7H_6(SO_2 \cdot S)_2 \cdot C_7H_6$, which is a white, amorphous powder insoluble in water. The action of chlorine on potassium toluene-2:4-disulphinate leads to the formation of toluene-2:4-disulphonic chloride; of bromine, to the formation of *toluene-2:4-disulphonic bromide*, which is a white solid and melts at 78°; and of iodine in potassium iodide solution, to oxidation to toluene-2:4-disulphonic acid.

Methyl toluene-2:4-disulphinate, formed by the action of methyl chlorocarbonate on the potassium salt, is a viscid, yellow oil.

Tolylene-2:4-bismethylsulphone, $C_7H_6(SO_2Me)_2$, crystallises in white leaflets and melts at 153—154°; the *bisethylsulphone* separates from ether sometimes in crystals, sometimes as an oil; the *bis-n-propylsulphone* separates from alcohol in right-angled crystals and melts at 83—84°; the *bisbutylsulphone* is a viscid, yellow oil; the *bisallylsulphone* crystallises in white leaflets and melts at 89—90°.

Tolylene-2:4-bisacetonylsulphone crystallises in yellowish-white, prismatic needles and melts at 127°. *Ethyl tolylene-2:4-bis-sulphoneacetate* is a viscid, yellow oil; the free *acid* is an oil; the *barium* salt is a white powder. *Tolylene-2:4-bis-sulphonacetamide* crystallises in white needles and melts and decomposes at 230°. *Ethyl tolylene-2:4-bis-*

sulphonebutyrate and the free acid are yellow oils; the barium salt crystallises in white leaflets.

Naphthalene-2:7-disulphinic acid, prepared from Ebert and Merz's naphthalenedisulphonic chloride (*Ber.*, 1876, 9, 597), is a solid, has bleaching properties like the other disulphinic acids. When heated with methyl iodide, the potassium salt yields *naphthalene-2:7-bismethylsulphone*, which is an amorphous substance. G. Y.

Triphenylmethyl Acetate. MOSES GOMBERG and G. T. DAVIS (*Ber.*, 1903, 36, 3924—3927. Compare Abstr., 1902, i, 534).—*Triphenylmethyl acetate*, $\text{CPh}_3\cdot\text{OAc}$, prepared by the action of silver acetate on triphenylchloromethane in benzene or ether, crystallises from light petroleum or ethyl acetate, and melts at $87-88^\circ$. When dissolved in acetyl chloride, it is at once converted into triphenylchloromethane; as Allen and Kölliker (Abstr., 1885, 655) and Herzig and Wengraf (Abstr., 1901, i, 702) used acetyl chloride in preparing their so-called triphenylmethyl acetate, it is obvious that their substance could not have been the real acetate; it was probably triphenylchloromethane. The authors show that this substance only is formed by the interaction of acetyl chloride and triphenylcarbinol ethyl ether, and that triphenylcarbinol is not attacked by acetic anhydride. W. A. D.

Existence of a Class of Substances Analogous to Triphenylmethyl. MOSES GOMBERG (*Ber.*, 1903, 36, 3927—3930. Compare Abstr., 1902, i, 534, 600).—The action of silver, zinc, or mercury on tri-*p*-tolylchloromethane, phenyl-di-*p*-tolylchloromethane, tri-*p*-nitrotriphenylchloromethane, or tri-*p*-anisylchloromethane is similar to the action of the same metals on triphenylchloromethane; in every case, a colour is first imparted to the liquid, probably owing to the formation of a coloured radicle similar to triphenylmethyl. The colours vary with the different substances, and soon disappear owing to the oxidation of the product first formed to substances analogous to, but more complex than, triphenylmethyl peroxide. W. A. D.

Gradual Synthesis of the Benzene Ring. MAURICE DELACRE and LOUIS GESCHÉ (*Bull. Acad. Roy. Belg.*, 1903, 735—756. Compare Abstr., 1902, i, 774).—The authors now find that the hydrocarbon, which they named dypnopinalcolene (Abstr., 1900, i, 603), and to which they ascribed the formula $\text{C}_{32}\text{H}_{26}$, is identical with the hydrocarbon, $\text{C}_{25}\text{H}_{22}$, obtained by the action of potassium hydroxide dissolved in alcohol on dypnone (Gesché, Abstr., 1901, i, 604). This melts at 98° , boils at $292-295^\circ$ under 40 mm. pressure, and is soluble in alcohol, benzene, or acetic acid; from the latter, it separates in a mixture of leaflets and needles. When reduced by sodium amalgam, it is converted into a mixture of two isomeric hydrocarbons, $\text{C}_{25}\text{H}_{24}$, one of which crystallises from alcohol in silky needles, melts at 145° , boils at $275-280^\circ$ under 27 mm. pressure, is soluble in ether (2.7 per cent.), boiling alcohol (1.5 per cent.), and cold alcohol (0.13 per cent.), and is partially converted by distillation under atmospheric pressure into its isomeride. The latter separates from alcohol in vitreous crystals and from light petroleum in large leaflets and melts at about 115° . It

dissolves in ether (3·7 per cent.), boiling alcohol (2·5 per cent.), and cold alcohol (0·22 per cent.), but these constants are probably influenced by the presence in the material employed of a small amount of the less fusible isomeride. When distilled under atmospheric pressure, it is partially converted into its isomeride. When the hydrocarbon, $C_{25}H_{22}$, is treated with bromine dissolved in carbon disulphide, it is converted into a *bromo-derivative*, $C_{25}H_{19}Br$; this forms large, transparent crystals, melts at 140° , boils at 360° , and is soluble in benzene and chloroform. It is not attacked by potassium hydroxide in alcohol, but is slowly reduced by sodium amalgam in presence of alcohol, forming a *substance* which crystallises in minute needles and melts at $88-89^{\circ}$.

The hydrocarbon, $C_{25}H_{22}$, and its reduction products, when reduced with hydriodic acid, furnish a mixture of two crystalline *hydrocarbons*, $C_{25}H_{26}$, and a small quantity of a *hydrocarbon* volatile in steam and possessing an odour like that of ethylbenzene.

On distillation, the hydrocarbon, $C_{25}H_{22}$, and its reduction products furnish triphenylbenzene and a mixture of volatile hydrocarbons (compare Abstr., 1900, i, 603).

T. A. H.

Dibromosulphonaphthalic Acid. GUIDO BARGELLINI (*L'Orosi*, 1902, 25, 289—293).—The acid containing sulphur and bromine, previously mentioned by Francesconi and the author (*Gazzetta*, 1902, 32, ii, 78; Abstr., 1903, i, 34) is found to be a *dibromosulphonaphthalic acid*, $SO_3H \cdot C_{10}H_3Br_2(CO_2H)_2$, and is best prepared by heating naphthalic anhydride with fuming sulphuric acid at $70-80^{\circ}$ for three hours, during which bromine is gradually added, the whole being then heated for an hour at 100° and for 4 hours at 200° . It crystallises in white needles melting at $204-205^{\circ}$, dissolves in water, ethyl acetate, methyl or ethyl alcohol or acetic acid, and, to a slight extent, in ether or benzene; it is soluble also in dilute aqueous solutions of alkali hydroxides or carbonates or ammonia. The composition of its *barium* salt ($+8H_2O$) shows the acid to be tribasic. The acid dissolves readily in concentrated sulphuric acid, giving a yellow solution exhibiting no fluorescence. When heated with resorcinol, in molecular proportion, in presence of zinc chloride, the acid gives the corresponding fluorescein, which dissolves in dilute sodium hydroxide solution giving a dark orange coloured solution, showing a green fluorescence less intense than that exhibited by the fluorescein of either naphthalic or bromonaphthalic anhydride; this alkaline solution dyes silk a brick-red colour.

T. H. P.

Application of Pyridine in the Preparation of some Amide Derivatives. PAUL FREUNDLER (*Compt. rend.*, 1903, 137, 712—714).—Secondary and tertiary amides may be prepared by the action of acyl chlorides on amides and anilides in presence of pyridine. The reaction takes place readily with aromatic acyl chlorides; the temperature must be kept low when fatty chlorides are employed, on account of their action on pyridine.

Dibenzanilide melts at 164° when pure (compare Kay, Abstr., 1894,

i, 77). The supposed isomeride of lower melting point (Higgin, Trans., 1882, 41, 132) is a mixture of the two benzoyl derivatives.

The following new compounds have been prepared : *p*-toluoyl-*o*-hydrazotoluene, melting at 132°, and reacting with benzoyl chloride to form benzoyl-*p*-toluoyl-*o*-hydrazotoluene, melting at 182°; benzoyl-*p*-toluoylaniline, melting at 159—160°; benzoylbenzenesulphanilide, melting at 114°; dibenzenesulphanilide, melting at 143—144°; isobutyrylacetamide, melting at 177—178°; and isobutyrylacetanilide, melting at 49—50°.

C. H. D.

Action of Aromatic Amines on Ethylenedisulphonic Chloride. Derivatives of Vinylsulphonic Acid. WILHELM AUTENRIETH and JULIUS KOBURGER (*Ber.*, 1903, 36, 3626—3634).—Aniline and ethylenedisulphonic chloride interact to form vinylsulphanilide and sulphur dioxide (Autenrieth and Rudolph, *Abstr.*, 1902, i, 22). This reaction takes place only with $\alpha\beta$ -disulphonic chlorides, and has now been extended in order to determine the influence of substitution in the amine employed on the course of the action. *o*-, *m*-, and *p*-Toluidines, *m*-nitroaniline, *m*-chloroaniline, and *p*-phenetidine behave towards ethylenedisulphonic chloride like aniline; *o*-, *m*-, and *p*-toluidines react with equal readiness to give quantitative yields of the corresponding vinylsulphonoluidides, but *m*-nitroaniline, owing to its positive nitro-group, does not readily react, whilst the weak base, *o*-nitroaniline, does not react at all.

The vinylsulphonanilides prepared are acid in character, being readily soluble in aqueous solutions of alkalis, from which they are reprecipitated on the addition of acid. They are readily alkylated and acetylated, but cannot be benzoylated.

Vinylsulphon-p-toluidide, $\text{CH}_2\text{:CH}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, prepared by the action of *p*-toluidine on ethylenedisulphonic chloride in benzene solution, separates from dilute alcohol in glistening, white leaflets and melts at 74°. Its *acetyl* derivative crystallises from dilute alcohol in glistening leaflets and melts at 87°.

Vinylsulphon-o-toluidide separates from dilute alcohol in leaflets and melts at 64—65°. Its *acetyl* derivative separates from dilute alcohol in fine prisms and melts at 69°.

Vinylsulphon-m-toluidide separates from dilute alcohol in prisms and melts at 88°.

Vinylsulphon-m-nitroanilide, $\text{CH}_2\text{:CH}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, prepared by boiling a concentrated benzene solution of *m*-nitroaniline and ethylenedisulphonic chloride for 1 hour, separates from dilute alcohol in yellow prisms and melts at 119°.

Vinylsulphon-p-phenetidine, $\text{CH}_2\text{:CH}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$, separates from water or dilute alcohol in glistening, white leaflets and melts at 88°. Its *acetyl* derivative forms slender prisms and melts at 70°.

Vinylsulphon-o-nitro-p-phenetidine, prepared by nitrating vinylsulphon-*p*-phenetidine, forms yellow prisms and melts at 92°. When reduced by zinc dust, it forms *m*-ethoxy-*o*-phenylenediamine, which condenses with benzil to form *m*-ethoxydiphenylquinoxaline.

When excess of bromine acts on vinylsulphonanilide, tribromoaniline and the additive compound, $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{SO}_2\cdot\text{NHPh}$, are formed

(compare Autenrieth and Rudolph, *loc. cit.*). This action proceeds in two stages, firstly, the simple addition of bromine to the sulphon-anilide, and secondly, the decomposition of the latter additive compound with evolution of hydrogen bromide. With vinylsulphon-*p*-phenetidine, the main action consists in the addition of bromine. *Dibromoethylsulphon-p-phenetidine*, $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$, separates from dilute alcohol in colourless, glistening prisms and melts at 139° ; when hydrolysed by concentrated hydrochloric acid, it forms *p*-phenetidine and not a dibromophenetidine, thus showing that the bromine has not been substituted in the benzene ring.

A. McK.

Condensation of Mercaptans with Nitriles. WILHELM AUTENRIETH and A. BRÜNING (*Ber.*, 1903, 36, 3464—3469).—*Benziminiothiophenyl ether*, $\text{NH}\cdot\text{CPh}\cdot\text{SPh}$, prepared by condensing benzonitrile and thiophenol with dry hydrogen chloride, separates from ether in well-formed prisms and melts at 48° ; the *hydrochloride* melts and decomposes at 178° , liberating hydrogen chloride, and dissolves unchanged in cold water, but is completely decomposed on boiling the solution.

Acetiminiothiophenyl ether, $\text{NH}\cdot\text{CMe}\cdot\text{SPh}$, was obtained as an unstable syrup; the *hydrochloride* melts and decomposes at 120° .

Propioniminiothiophenyl ether, $\text{NH}\cdot\text{CEt}\cdot\text{SPh}$, was only isolated as the *hydrochloride*, which is soluble in water, but begins to decompose at once.

Phenylacetiminiothiophenyl ether, $\text{NH}\cdot\text{C}(\text{CH}_2\text{Ph})\cdot\text{SPh}$, separates in white needles, but soon decomposes into its constituents; the *hydrochloride* separates in white crystals and melts at 158° .

The *hydrochloride* of *succiniminiothiophenyl ether*, $\text{C}_2\text{H}_4[\text{C}(\text{:NH})\cdot\text{SPh}]_2$, melts at 145° and is slowly decomposed by cold water.

Succiniminodithioethylene ether, $\text{CH}_2\cdot\text{C}(\text{NH})\cdot\text{S}\cdot\text{CH}_2$, was obtained as a yellow syrup, which gradually solidified; the mono-*hydrochloride*, $\text{C}_6\text{H}_{11}\text{N}_2\text{S}_2\text{Cl}$, is an amorphous, dark green powder, soluble in water, which dyes silk and wool, but the aqueous solution soon deposits yellow flocks, and the dyed fabric, although stable to light, is turned yellow by alkalis.

Formiminiothiophenyl ether, $\text{NH}\cdot\text{CH}\cdot\text{SPh}$, was only isolated as its *hydrochloride*, which is very soluble in water but soon decomposes.

T. M. L

***p*-Nitroaminodiphenylamine.** HEINRICH SCHOTT (D.R.-P. 145061).—*p*-Dinitrodiphenylamine may be reduced by warming with a solution of sodium sulphide, with or without the addition of sodium hydroxide or sulphur, forming *p*-nitro-*p*-aminodiphenylamine, a brown, crystalline powder, dissolving in alcohol or dilute hydrochloric acid and forming a soluble diazonium compound. *p*-Dinitrodiphenylnitrosoamine may be reduced in the same manner. The *p*-nitro-*o*-amino-compound, a small quantity of which is produced at the same time, is not diazotisable, and the reduction product may therefore be employed directly in the preparation of azo-dyes.

C. H. D.

d 2

Reduction of 2:5-Dimethylbenzaldazine and the Preparation of some Salts [of 2:5-Dimethyldibenzylamine]. EVERHART PERCY HARDING and LILLIAN COHEN (*J. Amer. Chem. Soc.*, 1903, 25, 1091—1093).—When 2:5-dimethylbenzaldazine is reduced with zinc dust and acetic acid, dimethyldibenzylamine is produced. The *hydrochloride*, *picrate*, *mercurichloride*, and *platinichloride* are described.

E. G.

Existence of Miller and Plöchl's Stereoisomeric Anils. ALEXANDER EIBNER (*Annalen*, 1903, 329, 210—224. Compare Abstr., 1901, i, 640).—[With M. AMANN.]—In order to ascertain whether the anhydro-compound obtained from propaldehyde and aniline (Sender's base) was a di-secondary base analogous to the anhydro-bases previously investigated (*loc. cit.*) or a secondary-tertiary base, a series of reactions have been studied.

The base could not be reduced by sodium and amyl alcohol, and is accordingly neither a di-secondary or a secondary-tertiary base, but more probably contains an azomethine group, $\text{H}\cdot\text{C}\cdot\text{N}\cdot$.

The *benzoyl* derivative of Sender's base, $\text{C}_{19}\text{H}_{21}\text{N}_2\text{Bz}$, forms large, cubic crystals with 1 mol. of alcohol, which belong to the rhombohedral system [$a:c=1:0\cdot3670$]; when free from alcohol, it melts at 144° and is remarkably stable, resisting three hours' boiling with concentrated acids. Unlike Eckstein's base (*loc. cit.*), it does not yield a nitrosoamine, a fact which shows that an anilino-group is no longer present. Since the azomethine group is able to form additive products, it is probable that benzoyl chloride is first added on, and then a ring produced with the elimination of hydrogen chloride, thus:

$$\begin{array}{c} \text{CHMe}\cdot\text{CH}\cdot\text{NPhBz} \\ | \\ \text{CHEt}\cdot\text{NPh} \end{array}$$

When propylideneaniline is treated with hydrogen chloride in ethereal solution, an unstable *dihydrochloride*, $\text{C}_{16}\text{H}_{22}\text{N}_2\cdot 2\text{HCl}$, is produced, which loses hydrogen chloride, becoming converted into a *hydrochloride*, $\text{C}_{16}\text{H}_{22}\text{N}_2\cdot\text{HCl}$; this behaviour indicates the presence of an azomethine group.

Since bromine forms, with the azomethine group of benzylideneaniline, an unstable additive product, which decomposes, yielding *p*-bromoaniline and benzaldehyde, it was probable that a similar behaviour would be observed in the case of this base; no additive product was isolated, but 2:6-dibromoaniline and other brominated anilines were formed.

With nitrous acid, a very unstable nitrosoamine is formed; in the absence of water, when nitrous fumes, dried by phosphoric oxide, are passed into a chloroform solution of the base, benzenediazonium nitrate is formed. With benzylideneaniline, a similar decomposition takes place, but in this case benzylideneaminoazobenzene is also produced. Neither the dinitrosoamines of Eckstein's nor Eibner's base showed this tendency to decompose with the formation of diazonium salts. On investigating the *dinitrosoamine* of the base obtained from acetaldehyde and *p*-toluidine, $\text{C}_{18}\text{H}_{20}\text{O}_2\text{N}_4$ (which crystallises in pale yellow needles melting at 165°), and the *dinitrosoamine* of the base prepared from acetaldehyde and *as-m*-xylidine, $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_4$ (which

forms yellow needles melting at $79-80^{\circ}$, it was found that in neither case was diazonium salts formed. Both these bases are accordingly compounds of the type $\text{NHar}\cdot\text{CHMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{NHar}$, whereas Sender's base is represented by the formula $\text{NPh}\cdot\text{CHEt}\cdot\text{CHMe}\cdot\text{CH}\cdot\text{NPh}$.

K. J. P. O.

Problem of Activity in connection with Asymmetric Nitrogen. EDGAR WEDEKIND (*Zeit. physikal. Chem.*, 1903, 45, 235—248. Compare Abstr., 1899, i, 351; 1900, i, 155).—The author has determined the most favourable conditions for the resolution of α -phenylbenzylmethylallylammonium iodide into its active constituents with the aid of *d*-camphorsulphonic acid (see Pope and Peachey, *Trans.*, 1899, 75, 1127; Pope and Harvey, *Trans.*, 1901, 79, 828). The same lines have been followed in an attempt to resolve *p*-tolylbenzylmethylallylammonium iodide and *p*-tolylmethylethylallylammonium iodide, but without success in either case.

Pope and Harvey observed (p. 831, *loc. cit.*) that a freshly prepared chloroform solution of active phenylbenzylmethylallylammonium iodide gradually became inactive, and they attributed this to a dissociation into benzyl iodide and methylallylaniline. Boiling point determinations, with chloroform as solvent, have been made to further elucidate this point, and the molecular weight found is less than one-third of the normal value. Similar experiments with *p*-tolylmethylethylallylammonium iodide gave a molecular weight more than half the normal value.

As shown previously by the author (Abstr., 1900, i, 155), benzylphenylmethylallylammonium salts undergo hydrolysis when their aqueous solutions are heated. By measuring the conductivity of phenylbenzylmethylallylammonium, *p*-tolylbenzylmethylallylammonium, and *p*-tolylmethylethylallylammonium *d*-camphorsulphonates in aqueous solution before and after heating, an idea of the relative stability of these substances may be obtained, for the acid liberated by hydrolysis (if such takes place) causes a marked increase in the conductivity. It has thus been found that the *p*-tolylbenzylmethylallylammonium salt is more stable than the phenylbenzylmethylallylammonium salt, whilst the *p*-tolylmethylethylallylammonium salt is hydrolysed only to a very slight extent. It is all the more remarkable that this salt has not been obtained in the active form.

It is noted, finally, that the resolution of phenylbenzylmethylallylammonium salt can be effected only with the aid of *d*-camphorsulphonic acid; the other methods usually employed are ineffective. J. C. P.

Phenylmethylethylallylammonium Iodide. EDGAR WEDEKIND (*Ber.*, 1903, 36, 3791—3796).—As the preparation of the halogen salts of phenylbenzylmethylallylammonium in three different ways (Abstr., 1899, i, 351; 1900, i, 155) had shown that it exists in two different isomeric modifications, the same methods have been applied to the preparation of a lower homologue. A mixture of methyl-ethylaniline and allyl iodide soon solidifies to a crystalline mass; recrystallised from chloroform, *phenylmethylethylallylammonium iodide* forms glistening plates belonging to the rhombic system [$a:b:c=$

0.9115:1:0.7208], containing a molecule of the solvent and melting indistinctly at 75—80°. The well-characterised *platinichloride* crystallises from boiling water in long, reddish-yellow needles melting just above 182°.

Ethylallylaniline and methyl iodide unite to an amorphous substance different from that just described, but converted into it on treatment with chloroform; it forms an identical *platinichloride*. Methylallylaniline and ethyl iodide unite to give an exactly similar, amorphous compound. The corresponding bromide forms colourless crystals, isomorphous with the iodide, which decompose at 140°.

E. F. A.

Nitric Oxide and Grignard's Reagent. JULIUS SAND and FRITZ SINGER (*Annalen*, 1903, 329, 190—194. Compare Abstr., 1902, i, 851).—Although both uranyl chloride, UO_2Cl_2 , and chromyl chloride react readily with magnesium alkyl haloids, the compounds produced are unstable and decomposed by water.

Nitric oxide forms an additive product with magnesium phenyl bromide, and appears to act as if it were dimolecular, N_2O_2 ; thus, $\text{N}_2\text{O}_2 + \text{MgPhBr} \rightarrow \text{ON} \cdot \text{NPh} \cdot \text{O} \cdot \text{MgBr} \rightarrow \text{ON} \cdot \text{NPh} \cdot \text{OH}$. Bromobenzene was allowed to interact with magnesium powder in the presence of ether, and pure nitric oxide led in after the air had been displaced from the vessel by means of hydrogen; the product was poured on to ice and the solution extracted with ether. The β -phenylnitrosohydroxylamine thus obtained melted at 59° and was identical with the nitrosoamine prepared by Bamberger (Abstr., 1894, i, 412); at the same time, a small quantity of diphenyl was isolated from the product of the reaction.

Nitrosomethylhydroxylamine was obtained in the form of its copper salt by the interaction of magnesium methiodide and nitric oxide; after the primary product of the reaction had been poured on to ice, copper oxide was added and the blue solution evaporated; the *copper* salt $(\text{N}_2\text{Me}_2\text{O}_2)_2\text{Cu}, \frac{1}{2}\text{H}_2\text{O}$, which is soluble in water and benzene, crystallises from aqueous alcohol in long, azure-blue needles

K. J. P. O.

Carbamide Oximes. JULIUS VON BRAUN and RUDOLF SCHWARZ (*Ber.*, 1903, 36, 3660—3663).—The cyanogen group in cyanoamides has the same additive power as the same group in nitriles, since cyanoamides form amides, thioamides, iminoethers, and amidines. The behaviour of cyanoamides towards hydroxylamine has now been studied.

Mono-substituted cyanoamides react with hydroxylamine very vigorously, but no definite compounds were isolated as products of the action. Disubstituted cyanoamides unite with hydroxylamine in molecular proportions.

Phenylmethylcyanoamide in methyl alcoholic solution unites with hydroxylamine to form the *oxime*, $\text{NMePh} \cdot \text{CN}, \text{NH}_2 \cdot \text{OH}$, which melts at 102°; it is a weak base and crystallises unchanged from its solution in aqueous hydrochloric or sulphuric acid. Its *hydrochloride*, prepared by passing hydrogen chloride into its ethereal alcoholic solution,

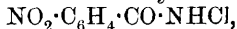
forms a snow-white powder and melts at 189° ; its *picrate* melts at $120-121^{\circ}$.

Dipropylecyanoamide unites with hydroxylamine to form the *oxime*, $\text{NPr}_2\cdot\text{CN}\cdot\text{NH}_2\cdot\text{OH}$, which melts at 115° ; the *picrate* of the latter melts at 185° .

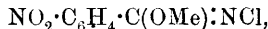
Diphenylcyanoamide in a similar manner forms the *oxime*, $\text{NPh}_2\cdot\text{CN}\cdot\text{NH}_2\cdot\text{OH}$, which melts at 161° ; its *hydrochloride* melts at $169-170^{\circ}$, whilst its *picrate* softens at 165° and melts completely at 182° .

These oximes are most probably carbamide derivatives of the type $\text{NR}_2\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{NH}_2$. A. McK.

The Beckmann Rearrangement. III. Stereoisomeric Chloroimino-acid Ethers. JULIUS STIEGLITZ and RICHARD B. EARLE (*Amer. Chem. J.*, 1903, 30, 399—412. Compare Abstr., 1897, i, 43, and 1903, i, 235).—*m*-Nitrobenzoylchloroamide,



obtained by the action of sodium hypochlorite on nitrobenzamide, crystallises from a mixture of acetone and benzene and melts at $183-184^{\circ}$. When this compound is treated with diazomethane, the α -modification of methyl chloroimino-*m*-nitrobenzoate,



is produced, which crystallises in long prisms or rectangular plates, melts at $86.5-87.5^{\circ}$, and is readily soluble in chloroform, benzene, or acetone; by the action of hydrogen chloride, it is converted into the hydrochloride of methyl imino-*m*-nitrobenzoate.

When the hydrochloride of methyl imino-*m*-nitrobenzoate is added to a large excess of sodium hypochlorite at 30° , a product is obtained consisting of a mixture of the α - and β -modifications of methyl chloroimino-*m*-nitrobenzoate, which may be separated by repeated crystallisation from a mixture of chloroform and light petroleum. The β -modification crystallises in thin, rhombohedral plates, melts at $81-82^{\circ}$, and by the action of dry hydrogen chloride is converted into methyl iminonitrobenzoate.

The molecular weight of each modification was determined by the cryoscopic method and found to agree with that required by the formula $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{OMe})\cdot\text{NCl}$. Both isomerides are stable compounds and remain unchanged when heated for some time at 80° , or even for a few minutes at 140° . The change of one isomeride into the other has never been observed. Physical and structural isomerism being excluded, it follows that the compounds must be stereoisomerides, one being the *syn*-modification, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\overset{\text{OMe}}{\underset{\text{Cl}\cdot\text{N}}{\text{C}}}$, and the other the *anti*-modification, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\overset{\text{OMe}}{\underset{\text{N}\cdot\text{Cl}}{\text{C}}}$.

m-Nitrobenzoylmethylchloroamide, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NClMe}$, prepared by the action of chlorine on *m*-nitrobenzoylmethylamide, crystallises in thick, monoclinic prisms, melts at $76-77^{\circ}$, and when treated with dry hydrogen chloride is reconverted into *m*-nitrobenzoylmethylamide.

E. G.

The Beckmann Rearrangement. IV. The Formation of Acylalkylcarbamides in Hofmann's Reaction. JULIUS STIEGLITZ and RICHARD B. EARLE (*Amer. Chem. J.*, 1903, 30, 412—421).—It is found that, both in the aliphatic and aromatic series, acid chloroamides condense very readily with carbimides with formation of acylalkylcarbamides, whereas the acid amides do not respond at all to the action of carbimides. The formation of acylalkylcarbamides in Hofmann's reaction is therefore due to the ready condensation of a carbimide, the primary product of the rearrangement of a molecule of an acid halogen-amide, with a second molecule of the latter, and to a subsequent hydrolysis of the condensation product. The action is thus in harmony with the conception that a carbimide may always be considered to be the first product of the "Beckmann rearrangement" of an acid halogen-amide.

By the action of *p*-chlorophenylcarbimide on benzoylchloroamide, *s*-benzoyl-*p*-chlorophenylcarbamide, $C_6H_4Cl \cdot NH \cdot CO \cdot NHBz$, is obtained, which crystallises in white needles and melts at 235—237°. The same compound may be prepared by the action of *p*-chlorophenylcarbimide on benzamide and by the action of benzoyl chloride on *p*-chlorophenylcarbamide.

When a solution of phenylcarbimide in dry benzene is warmed with dry benzoylchloroamide, benzoyl-*p*-chlorophenylcarbamide is formed, the chlorine atom having migrated into the benzene nucleus. In the presence of alkali, phenylcarbimide reacts with benzoylchloroamide with formation of *s*-benzoylphenylcarbamide; this compound is also produced under the same conditions by the action of phenylcarbimide on benzoylbromoamide.

By the action of phenylcarbimide on acetylchloroamide, *s*-acetylphenylcarbamide is formed. Acetamide does not react with phenylcarbimide. Methylcarbimide reacts with acetylchloroamide with formation of *s*-acetylmethylcarbamide, but does not combine with acetamide.

Dibenzoylchloroamide, NBz_2Cl , obtained by the action of chlorine on the silver salt of dibenzamide, crystallises in white needles and melts at 86°. When heated, it shows no tendency to undergo a "Beckmann rearrangement," but is decomposed with formation of chlorine, benzonitrile, and benzoyl chloride. E. G.

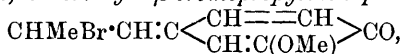
cycloHexanol. ARNOLD F. HOLLEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 201—203).—*cycloHexanol*, prepared by passing dry hydrogen through phenol heated at 160—170°, and then leading the resulting vaporous mixture over freshly reduced nickel at 140—160°, is a syrupy liquid and boils at 160—161°. It is oxidised by chromic acid to ketohexamethylene. A. McK.

Action of Oxygen on Magnesium Organo-haloid Compounds. LOUIS BOUVEAULT (*Bull. Soc. chim.*, 1903, [iii], 29, 1051—1054. Compare Grignard, *Abstr.*, 1900, i, 382; 1901, i, 679; and Zelinsky, 1902, i, 675).—When *cyclohexane* is converted by Grignard's method (*loc. cit.*) into *cyclohexanecarboxylic acid* (hexahydrobenzoic acid), about 20 per cent. of *cyclohexanol* (hexahydrophenol) is simultane-

ously produced, which, it is suggested, is formed by the action of atmospheric oxygen on the magnesium compound of the haloid derivative of *cyclohexane* employed (compare Bodroux, *Abstr.*, 1903, i, 249, and Taboury, *ibid.*, 748). The validity of this hypothesis was confirmed by the conversion of magnesium-benzyl chloride into benzyl alcohol by the action of oxygen. T. A. H.

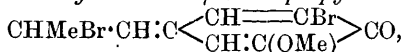
Action of Bromine and Chlorine on Phenols. **Action of Bromine on *iso*Eugenol (3-Methoxy-*p*-propylenephénol).** THEODOR ZINCKE and O. HAHN (*Annalen*, 1903, 329, 1—36).—The products of the action of bromine on *isoeugenol* are analogous to the substances obtained from *p*-vinylphenol (*Abstr.*, 1902, i, 615). Some of the derivatives of *isoeugenol* described in this paper have been previously prepared by Chasanowitz and Hell (*Abstr.*, 1885, 779), Hell and Portman (*Abstr.*, 1895, i, 657), and Auwers and Müller (*Abstr.*, 1902, i, 212).

*iso*Eugenol dibromide (ψ -3-methoxy-4- $\alpha\beta$ -dibromopropylphenol), prepared by adding an ethereal solution of bromine to an ethereal solution of *isoeugenol*, crystallises from benzene in large leaflets melting at 95° (Hell and Portman record 86—87°, and Auwers and Müller, 94—95°). On adding a few drops of sulphuric acid to its solution in acetic anhydride, the acetyl derivative (m. p. 125—126°) is formed. By the action of sodium carbonate on the ethereal solution of the dibromide, 2-methoxy-4- β -bromopropylidenequinone,

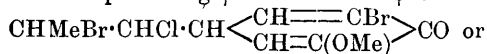


is formed as a yellow oil.

2-Bromo*isoeugenol* dibromide (ψ -2-methoxy-6-bromo-4- $\alpha\beta$ -dibromopropylphenol), prepared by brominating *isoeugenol* in ethereal solution, crystallises in needles melting at 138° (Auwers and Müller give 132—133°). 2-Methoxy-6-bromo-4- β -bromopropylidenequinone,



is prepared by treating an ethereal solution of the dibromide last mentioned with 10 per cent. aqueous sodium acetate; the ethereal solution assumes an intense yellow coloration and deposits the yellow prisms of the quinone, which sinters at 140° and decomposes at a higher temperature. The solutions in methyl or ethyl alcohol or acetic acid soon become colourless, whilst those in indifferent solvents become deep red. Under these conditions, probably polymeric quinones are formed. The quinone combines with hydrogen chloride and bromide producing ψ -chlorides and ψ -bromides; the ψ -chloride,



is prepared by digesting the quinone with an acetic acid solution of hydrogen chloride; it crystallises in colourless needles melting at 110° and is insoluble in alkali hydroxides.

6-Bromo*isoeugenol* is obtained when the bromo*isoeugenol* dibromide or the quinone prepared from it, is reduced by hydriodic acid; it

forms a soluble white powder which sinters on heating. Its *acetyl* derivative is an amorphous powder.

On dissolving the quinone above mentioned in methyl alcohol, *2-methoxy-6-bromo-4- α -methoxy- β -bromopropylphenol* is produced; it forms small, white needles, melting at 106—107° (Auwers, 104—105°), and is easily soluble in alkali hydroxides and carbonates. The corresponding ethoxypropyl compound crystallises in small, rhombic leaflets melting at 66—67° (Auwers, 78—80°). The corresponding hydroxy-compound, *2-methoxy-6-bromo-4- α -hydroxy- β -bromopropylphenol*, is formed whenever the quinone is exposed to moisture, even moist air; it forms colourless needles melting at 144° (Auwers, 135—136°); the *diacetyl* derivative forms small crystals melting at 112—114°.

2-Methoxy-6-bromo-4- α -acetoxy- β -bromopropylphenol is formed when the corresponding bromo-compound just mentioned is heated with sodium acetate in acetic acid solution, or when the quinone is shaken with acetic acid; it forms rhombic crystals melting at 85—86° and is decomposed by alkali hydroxides.

The *acetyl* derivative of 6-bromoisoeugenol dibromide is produced when the dibromide is boiled for a short time with acetic anhydride, or when *2-methoxy-6-bromo-4- α -hydroxy- β -bromopropylphenol* is heated with acetyl bromide, or finally by brominating *isoeugenol* acetate; it melts at 130—131°. The *acetyl* derivative of 6-bromo-4- α -chloro- β -bromopropylphenol, prepared by the action of acetyl chloride on the hydroxybromopropylphenol, crystallises in needles melting at 111—112°.

3 : 6-Dibromoisoeugenol dibromide (*2-methoxy-3 : 6-dibromo-4- α - β -dibromopropylphenol*), $\text{CHMeBr} \cdot \text{CHBr} \cdot \text{CH} \begin{smallmatrix} \text{CBr} : \text{C}(\text{OMe}) \\ \text{CH} = \text{CBr} \end{smallmatrix} \text{CO}$ or

$\text{CHMeBr} \cdot \text{CHBr} \cdot \text{C} \begin{smallmatrix} \text{CBr} : \text{C}(\text{OMe}) \\ \text{CH} = \text{CBr} \end{smallmatrix} \text{C} \cdot \text{OH}$, is easily prepared by treat-

ing the tribromoisoeugenol with bromine, and forms large, lustrous crystals melting at 124° and behaves as a ψ -bromide. On treatment with 10 per cent. aqueous sodium acetate, it is converted into *2-methoxy-3 : 6-dibromo-4- β -bromopropylidenequinone*,

$\text{CHMeBr} \cdot \text{CH} : \text{C} \begin{smallmatrix} \text{CBr} : \text{C}(\text{OMe}) \\ \text{CH} = \text{CBr} \end{smallmatrix} \text{CO}$, which crystallises in yellow plates,

begins to decompose at 175°, and melts at 200°; when dissolved in acetone, it is immediately converted into a white, amorphous substance, $\text{C}_{10}\text{H}_9\text{O}_2\text{Br}_3$, which is probably a polymeride.

3 : 6-Dibromoisoeugenol, $\text{C}_3\text{H}_5 \cdot \text{C}_6\text{HBr}_2(\text{OMe}) \cdot \text{OH}$, is readily prepared by reducing the tetrabromo-compound by zinc and hydrobromic acid in ethereal solution; it crystallises in long, colourless needles melting at 102°, soluble in sodium hydroxide, and combining with bromine directly to form the tetrabromo- ψ -bromide just described. The *acetyl* derivative forms crystals melting at 123°.

2-Methoxy-3 : 6-dibromo-4- α -methoxy- β -bromopropylphenol is obtained from the tetrabromo- ψ -bromide or from the corresponding quinone by treatment with methyl alcohol; it forms small crystals melting at 111—112°, and is soluble in alkali hydroxides. *2-Methoxy-3 : 6-dibromo-4- α -hydroxy- β -bromopropylphenol*, prepared in the same manner

as the hydroxy-compounds of similar constitution above described, forms cubic or octahedric crystals melting at 127—128°; the *diacetyl* derivative forms lustrous crystals melting at 139—140°. The corresponding *mono-acetyl* derivative, prepared by the action of acetic acid on the tetrabromo- ψ -bromide or on tribromopropylidenequinone, crystallises in colourless needles melting at 114—115°, and is converted by alkalis into an amorphous substance probably a quinone, and by acetic anhydride into the diacetyl derivative just described. On boiling the tetrabromo- ψ -bromide with acetic anhydride or on heating 3:6-dibromoisoeugenol dibromide under pressure at 100° with acetyl bromide, the *acetyl* derivative of the compound last mentioned is formed; it crystallises in colourless needles melting at 117—118°. The *acetyl* derivative of 3:6-dibromo-4- α -chloro- β -bromopropylphenol, prepared by the action of acetyl chloride on the dibromohydroxybromopropylphenol, crystallises in slender needles melting at 97—98°.

3:5:6-Tribromoisoeugenol dibromide (2-methoxy-3:5:6-tribromo-4- $\alpha\beta$ -dibromopropylphenol), $\text{CHBrMe}\cdot\text{CHBr}\cdot\text{CH}\begin{smallmatrix} \text{CBr}:\text{C}(\text{OMe}) \\ \text{CBr}=\text{CBr} \end{smallmatrix}\text{CO}$ or $\text{CHBrMe}\cdot\text{CHBr}\cdot\text{C}\begin{smallmatrix} \text{CBr}:\text{C}(\text{OMe}) \\ \text{CBr}=\text{CBr} \end{smallmatrix}\text{C}\cdot\text{OH}$, is prepared by heating mol. proportions of dibromoisoeugenol dibromide and bromine under pressure at 100°, and crystallises from benzene in needles melting at 130°.

2-Methoxy-3:5:6-tribromo-4- β -bromopropylidenequinone, prepared from the compound last mentioned by the action of sodium acetate when the conditions are carefully regulated, crystallises in yellow needles decomposing when heated. With hydrogen chloride and bromide, it forms colourless, additive products; the compound with hydrogen chloride, which is prepared by passing the dry gas into a suspension of the quinone in ether, forms cubic crystals melting at 102—103° and is insoluble in alkalis.

On reducing the pentabromo- ψ -bromide with hydrogen iodide in acetic acid solution, 3:5:6-tribromoisoeugenol is formed; it crystallises in silky needles melting at 118°, and readily forms additive compounds with bromine, hydrogen bromide, &c. When the pentabromo- ψ -bromide or the corresponding propylidenequinone is warmed with methyl alcohol, 2-methoxy-3:5:6-tribromo-4- α -methoxy- β -bromopropylphenol is obtained as a colourless, crystalline substance melting at 126—127°. The corresponding *acetoxy*-derivative, prepared by substituting acetic acid for methyl alcohol, crystallises in long needles melting at 156—157°. The *acetyl* derivative of tribromoisoeugenol dibromide is easily prepared by treating the pentabromo- ψ -bromide with acetic anhydride and then adding a few drops of sulphuric acid; it crystallises in needles melting at 175°.

K. J. P. O.

Interdependence of Acidity and Structure of Polycyclic Phenols. PAUL N. RAIKOW (*Chem. Zeit.*, 1903, 27, 1125—1127. Compare Abstr., 1903, i, 754).—The action of potassium hydroxide, potassium carbonate, potassium phosphate, ammonia, &c., on α -naphthol, β -naphthol, alizarin, purpurin, hexahydroxyanthraquinone, aurin, rosolic acid, phenolphthalein, fluorescein, eosin, iodoeosin, tetraiodotetra-

chlorofluorescein, nitroso- β -naphthol, dinitro- α -naphthol, and tetranitrodihydroxyanthraquinone was studied. The benzene ring, as a substituent in polycyclic phenols, exercises an acidifying influence, α -naphthol, for instance, being more acidic than phenol. In compounds with condensed benzene rings, the benzene ring substituent exerts a stronger acidifying influence the nearer it is to the hydroxyl grouping; thus α -naphthol is a stronger acid than β -naphthol. The further introduction of a hydroxyl grouping into a polycyclic phenol increases the acidity, thus, purpurin is more strongly acidic than alizarin. Aurin and rosolic acid are more strongly acidic than phenolphthalein and fluorescein. A. McK.

4-Hydroxy-3-methyltriphenylcarbinol [Diphenyl-6-hydroxy-*m*-tolylcarbinol]. AUGUSTIN BISTRZYCKI and B. ZURBRIGGEN (*Ber.*, 1903, 36, 3558—3564).—4-Hydroxy-3-methyltriphenylcarbinol (α -form), $\text{OH}\cdot\text{CPh}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OH}$, prepared by dissolving 4-hydroxy-3-methyltriphenylacetic acid in concentrated sulphuric acid at the ordinary temperature, crystallises from dilute acetic acid in lustrous, yellow prisms, melts and decomposes at $107\text{--}108^\circ$, and gives a *potassium* salt, $\text{C}_{20}\text{H}_{17}\text{O}_2\text{K}$, which crystallises in colourless, glistening leaflets. The *acetyl* derivative, $\text{OH}\cdot\text{CPh}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OAc}$, crystallises from glacial acetic acid and melts at $127\text{--}128^\circ$. The *m*-nitrobenzoyl derivative, $\text{OH}\cdot\text{CPh}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, prepared by the Lossen-Baumann method, crystallises from a mixture of benzene and light petroleum and melts at $118\text{--}119^\circ$. The *dimethyl ether*, $\text{OMe}\cdot\text{CPh}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OMe}$, prepared by passing hydrogen chloride through a solution of the carbinol in methyl alcohol, crystallises from methyl alcohol in microscopic plates and melts at $91\text{--}92^\circ$.

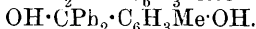
4-Hydroxy-3-methyltriphenylmethane [*Diphenyl-6-hydroxy-m-tolylmethane*], $\text{CHPh}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OH}$, prepared by reducing the corresponding carbinol with zinc and acetic acid, separates from dilute acetic acid in well-formed crystals and melts at 100° . The *acetyl* derivative forms colourless aggregates of prisms and melts at $63\text{--}64^\circ$; the *m*-nitrobenzoyl derivative crystallises from acetic acid in prismatic needles and melts at $93\text{--}94^\circ$. The *methyl ether*, $\text{CHPh}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OMe}$, crystallises from methyl alcohol in stellate aggregates of prisms and melts at $80\text{--}81^\circ$; the corresponding *ethyl ether* melts at 75° .

$\omega\omega$ -Diphenyl-2-methylquinomethane, $\text{CPh}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{O}$ (compare Auwers and Schröter, *Abstr.*, 1903, i, 820), is formed when the foregoing carbinol is heated for 3—4 hours at 180° ; it crystallises from benzene in microscopic plates and melts at 176° . W. A. D.

4-Hydroxy-3-methyltriphenylcarbinol [Diphenyl-6-hydroxy-*m*-tolylcarbinol] and *p*-Hydroxytriphenylcarbinol. AUGUSTIN BISTRZYCKI and CARL HERBST (*Ber.*, 1903, 36, 3565—3572). Compare preceding abstract and *Abstr.*, 1901, i, 701; 1902, i, 776; Auwers and Schröter, *Abstr.*, 1903, i, 820).— $\omega\omega$ -Diphenyl-2-methylquinomethane, on reduction with zinc and acetic acid, is converted almost quantitatively into 4-hydroxy-3-methyltriphenylmethane, and when boiled with 50 per cent. acetic acid yields 4-hydroxy-3-methyltriphenyl-

carbinol; on boiling with alcoholic sodium ethoxide and decomposing the product with carbon dioxide, it gives 4-hydroxy-3-methyltriphenylcarbinyl ethyl ether, $\text{OEt} \cdot \text{CPh}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{OH}$, which crystallises from a mixture of benzene and light petroleum in colourless, four-sided plates and melts at $150-151^\circ$.

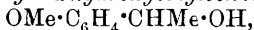
When ω -diphenyl-2-methylquinomethane is boiled with alcoholic potassium hydroxide and the product precipitated by dilute acetic acid, a substance apparently isomeric and not identical with 4-hydroxy-3-methyltriphenylcarbinol is obtained; it crystallises from benzene in colourless needles or flat prisms, melts at $148-149^\circ$, and only differs from its isomeride in not losing water at 100° , whereas the carbinol melting at $107-108^\circ$ begins to decompose at $50-60^\circ$, undergoing conversion into ω -diphenyl-2-methylquinomethane. It is called provisionally the β -form of the carbinol, and can be reconverted into the α -form by simply warming with acetic acid; attempts to acetylate it gave only the acetyl derivative of the α -form. Auwers and Schröter (*loc. cit.*) have considered the two corresponding forms of *p*-hydroxytriphenylcarbinol to differ by $\frac{1}{2}\text{H}_2\text{O}$, but the authors consider them to have the formulæ $\text{OH} \cdot \text{CPh}_2 \cdot \text{CH} : \text{C}_6\text{H}_3\text{Me} : \text{O}$ and



The remainder of the paper is largely a reply to Auwers and Schröter's criticisms, but the following result is noteworthy. When *p*-ethoxytriphenylcarbinyl ethyl ether is boiled with acetic anhydride, acetic acid, or acetyl chloride, or heated alone at 150° for 4 hours, it is converted into *p*-ethoxytriphenylmethane.

W. A. D.

Reduction of Unsaturated Phenol Ethers by Sodium and Alcohol. AUGUST KLAGES [with A. EPPELSHEIM] (*Ber.*, 1903, 36, 3584—3597).—2-Methoxy-1 α -hydroxyethylbenzene,



prepared by the action of magnesium methiodide on salicylaldehyde methyl ether, is a colourless, viscous liquid and boils at $119-120^\circ$ under 11 mm. pressure. The phenylurethane, $\text{C}_{16}\text{H}_{17}\text{O}_3\text{N}$, crystallises from alcohol in colourless needles and melts at 106° .

o-Methoxyacetophenone, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{COMe}$, boils at $120-121^\circ$ under 13 mm. and at 239° under 757 mm. pressure. The oxime, $\text{C}_9\text{H}_{11}\text{O}_2\text{N}$, forms colourless needles and melts at 83° . The phenylhydrazone, $\text{C}_{15}\text{H}_{11}\text{ON}_2$, crystallises from alcohol in stout, colourless, glistening tablets and melts at 114° . The semicarbazone, $\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}_3$, crystallises from alcohol in colourless needles and melts at $180-182^\circ$.

The chloride, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CHMeCl}$, was not purified but was converted into the pyridinium chloride, $\text{C}_5\text{NH}_5\text{Cl} \cdot \text{CHMe} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, which separates from a mixture of alcohol and ether in colourless crystals and melts at $119-121^\circ$; the corresponding picrate separates from alcohol in small, yellow crystals and melts at $146-147^\circ$.

o-Vinylanisole, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH}_2$, prepared by heating the chloride with pyridine at 115° , is a mobile, refractive oil, with a phenol-like odour, boils at $82-83^\circ$ under 11 mm. pressure, has a sp. gr. 1.0002 at $17/4^\circ$, n_D 1.556, and is converted into a resin either when distilled under atmospheric pressure, or slowly at the ordinary temperature. It is reduced by sodium and alcohol to *o*-ethylanisole, which boils at $70-71^\circ$.

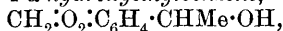
under 11 mm. and at 186—188° under 758 mm. pressure, has a sp. gr. 0.9636 at 19°/4°, and n_D 1.512.

3-Methoxy-1- α -hydroxyethylbenzene is a colourless oil which boils at 132—133° under 12 mm. pressure, has a sp. gr. 1.0781 at 19°/4°, and n_D 1.5325; the phenylurethane was obtained only as an oil. *m*-Methoxyacetophenone, prepared by oxidising the carbinol, yields a semicarbazone which crystallises from acetic acid in minute, colourless needles and melts at 181—183°. *m*-Vinylanisole is a mobile liquid which boils at 89—90° under 14 mm. pressure, is oxidised by permanganate, and has a great tendency to polymerise. When reduced, it yields *m*-ethylanisole, a colourless liquid which boils at 77—78° under 12 mm. and at 196—197° under 758 mm. pressure, has a sp. gr. 0.95746 at 18°/4°, and n_D 1.5102.

4-Methoxy-1- α -hydroxyethylbenzene, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CHMe} \cdot \text{OH}$, is a colourless oil and has a sp. gr. 1.086 at 16°/4°, and n_D 1.537; the phenylurethane, separates from alcohol in colourless needles and melts at 82—83°. *p*-Vinylanisole is a mobile liquid which boils at 90—91° under 13 mm. and at 204—205° under 756 mm. pressure, and has a sp. gr. 1.0001 at 13°/4°, and n_D 1.5642; Perkin gives b. p. 203—204°, sp. gr. 1.0029 at 15°. It is reduced to *p*-ethylanisole, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{Et}$, which boils at 79—80° under 13 mm. and at 195—197° under atmospheric pressure, and has a sp. gr. 0.9624 at 15°/4° and n_D 1.5094.

4-Ethoxy-1- α -hydroxyethylbenzene, $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{CHMe} \cdot \text{OH}$, distils at 140—142° under 11 mm. pressure, crystallises from light petroleum in needles, and melts at 48°; the phenylurethane, $\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}$, separates from alcohol in colourless flakes and melts at 81°. *p*-Vinylphenetole, $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CH}_2$, boils at 108—110° under 12 mm. pressure, has a sp. gr. 0.9764 at 18°/4°, and solidifies when cooled; it is reduced by sodium and alcohol to *p*-ethylphenetole, the sulphonic acid of which crystallises from benzene in plates and melts at 82—84° and the sulphonamide crystallises from dilute alcohol in colourless, glistening needles and melts at 118°.

3 : 4-Methylenedioxy-1- α -hydroxyethylbenzene,



is a clear, viscous oil, which boils at 137—138° under 14 mm. pressure, has a sp. gr. 1.2204 at 18°/4°, and n_D 1.5483; it does not solidify when cooled, and is oxidised by chromic acid to acetylpipecrone; the phenylurethane crystallises from alcohol in stout pyramids and melts at 65—67°. Vinylcatechol methylene ether, $\text{CH}_2 \cdot \text{O}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CH}_2$, is a mobile oil which boils at 107—108° under 15 mm. pressure, thickens when heated to 160° and becomes a hard glass when cooled; it has a sp. gr. 1.1488 at 18°/4°, n_D 1.5802, and is reduced by sodium and alcohol to ethylcatechol methylene ether, $\text{CH}_2 \cdot \text{O}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{Et}$, a colourless oil which boils at 92—93° under 17 mm. and at 212—213° under 759 mm. pressure.

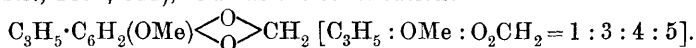
T. M. L.

Formation of Nitroso-compounds of Polyhydroxylic Phenols. JACQUES POLLAK (*Chem. Centr.*, 1903, ii, 829; from *Verh. Vers. Deutsch. Naturf. Aerzte*, 1902, ii, 1, 80—84).—It is not necessary to assume that in the formation of isonitroso-orcinol (Henrich, *Abstr.*, 1901, i, 464) the group NOH enters between two OH groups, for isonitroso-

orcinol may have a constitution, $\text{OC} \begin{smallmatrix} \text{CH}=\text{CMe} \\ \text{CH}:\text{C}(\text{OH}) \end{smallmatrix} \text{C}:\text{N}\cdot\text{OH}$, analogous to that of *isonitrosophloroglucinol* methyl ether (Abstr., 1903, i, 252). *isoNitroso-orcinol* monomethyl ether would then have the formula $\text{OMe}\cdot\text{C} \begin{smallmatrix} \text{CH}:\text{CMe} \\ \text{CH}-\text{CO} \end{smallmatrix} \text{C}:\text{N}\cdot\text{OH}$. The first $\text{N}\cdot\text{OH}$ group is thus placed, in accordance with Kostanecki's generalisation, in the ortho-position with regard to one OH group and in the para-position to the other; the second $\text{N}\cdot\text{OH}$ group would enter between two OH groups.

E. W. W.

Phenol Ethers. III. Constitution of Myristicin. HERMANN THOMS (*Ber.*, 1903, 36, 3446—3451).—Myristicin contains an allyl group in place of the butenyl group originally postulated by Semmler (Abstr., 1892, 311), and has the constitution:



When boiled with alcoholic potash, it is converted into *isomyristicin*, in which the allyl group is converted into a propenyl group; *isomyristicin* crystallises from dilute alcohol in small, colourless prisms and melts at 44—45°; Semmler's myristicin had been heated with sodium in the course of preparation, solidified when cooled, and gave a crystalline dibromide; it is therefore probable that it consisted largely of *iso*-myristicin; the myristicin used in the present research could not be crystallised and did not give a crystalline dibromide. A small quantity of the phenol, $\text{C}_3\text{H}_5\cdot\text{C}_6\text{H}_2(\text{OMe})(\text{OH})\cdot\text{O}\cdot\text{CH}_2\cdot\text{OEt}$, is produced with the *isomyristicin*.

isoMyristicin dibromide, $\text{CHMeBr}\cdot\text{CHBr}\cdot\text{C}_6\text{H}_2(\text{OMe})\cdot\text{O}_2\cdot\text{CH}_2$, prepared by the action of bromine on an ethereal solution of *isomyristicin* at -18°, crystallises from light petroleum in silky needles and melts at 109°.

Dibromomyristicin dibromide, $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_2(\text{OMe})\cdot\text{O}_2\cdot\text{CH}_2$, separates from alcohol as a white, crystalline powder and melts at 130°. *Dibromoisomyristicin dibromide*, $\text{C}_3\text{H}_5\text{Br}_2\cdot\text{C}_6\text{H}_2(\text{OMe})\cdot\text{O}_2\cdot\text{CH}_2$, crystallises from alcohol in colourless needles and melts at 156°.

Dihydromyristicin, $\text{OMe}\cdot\text{C}_6\text{H}_2\text{Pr}^a\cdot\text{O}_2\cdot\text{CH}_2$, boils at 149—150° under 17 mm. pressure. *5-Methoxy-3-propylphenol*, $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Pr}^a\cdot\text{OH}$, produced as a by-product in the reduction, boils at 160—161° under 17 mm. pressure, and has a sp. gr. 1·0598 at 20°. Its methyl ether, *3:5-dimethoxypropylbenzene*, $\text{C}_6\text{H}_3\text{Pr}^a(\text{OMe})_2$, boils at 136—137° under 16 mm. pressure, has a sp. gr. 1·0194 at 19°, and is isomeric with dihydromethyleugenol.

isoMyristicin is oxidised by potassium permanganate to Semmler's myristicinaldehyde and myristic acid.

T. M. L.

Phenol Ethers. IV. The Phenol Ether of the Essential Oil of French Parsley Seeds. HERMANN THOMS (*Ber.*, 1903, 36, 3451—3456).—The German oil solidifies when cooled owing to separation of apiole, but the French oil, a mobile, pale-yellow, fragrant liquid of sp. gr. 1·017, and $[\alpha]_D -5\cdot7^\circ$ at 20°, remains liquid. Sodium carbonate extracts from the latter 0·0804 per cent. of palmitic acid,

whilst potassium hydroxide extracts 0.0516 per cent. of mixed phenols; sodium hydrogen sulphite separates only traces of aldehydes and ketones. The residue was fractionally distilled at first under atmospheric and then under reduced pressures. The first fraction consisted chiefly of pinene, but the third fraction yielded a tetrabromide, $\text{OMe}\cdot\text{C}_{10}\text{H}_7\text{O}_2\text{Br}_4$, identical with dibromomyristicin dibromide, and gave crystals of isomyristicin when heated with alcoholic potash; it therefore consists largely of myristicin; the small sixth fraction, when cooled, yielded crystals of apiole (methoxymyristicin).

Both the French and the German oils are obtained from *Petroselinum sativum* (parsley); the German fruit is slightly smaller than the French, but has exactly the same anatomical structure; the production of apiole in one case and myristicin in the other is perhaps due to differences in cultivation.

T. M. L.

Preparation of Pentahydroxybenzene. FRANZ WENZEL and HUGO WEIDEL (*Chem. Centr.*, 1903, ii, 829—830; from *Verh. Vers. Deut. Naturf. Aerzte*, 1902, ii, 1, 88—89).—When the diethyl ether of styphnic acid, prepared by the action of nitro-sulphuric acid on resorcinol diethyl ether, is reduced by means of tin and hydrochloric acid, triaminoresorcinol diethyl ether is formed, and this substance, when boiled with water, yields the diethyl ether of pentahydroxybenzene. *Pentahydroxybenzene*, prepared by the action of hydriodic acid on the diethyl ether, crystallises from concentrated hydriodic acid in colourless crystals and is very readily soluble in water, but almost insoluble in organic solvents.

E. W. W.

Abnormal Condensation of Trioxymethylene and certain Aromatic Organomagnesium Compounds. MARC TIFFENEAU and RAYMOND DELANGE (*Compt. rend.*, 1903, 137, 573—575. Compare Abstr., 1903, i, 819).—The alcohol obtained by condensing trioxymethylene and magnesium benzyl chloride is not the normal product, benzylcarbinol, as stated by Grignard (Abstr., 1902, i, 198), but the isomeric *o*-tolylcarbinol. The two alcohols have similar boiling points, that of *o*-tolylcarbinol being 219° under the ordinary pressure and $119\text{--}120^\circ$ under 14—15 mm.; but whereas *o*-tolylcarbinol is a crystalline solid melting at 35° , benzylcarbinol is a liquid which does not solidify at -20° . The phenylurethane derivative of *o*-tolylcarbinol melts at 79° , that of benzylcarbinol at 80° , whilst a mixture of the two melts at 70° .

This abnormal reaction between trioxymethylene and magnesium benzyl chloride is not due to the latter reacting as its isomeride, magnesium *o*-tolyl chloride $\text{C}_6\text{H}_4\cdot\text{Me}\cdot\text{MgCl}$, because on treatment with carbon dioxide it gives a yield of 60 per cent. of phenylacetic acid, according to the equation $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{MgCl} + \text{CO}_2 + \text{H}_2\text{O} = \text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CO}_2\text{H} + \text{MgCl}\cdot\text{OH}$. The authors therefore suggest that this particular condensation is of the same type as that whereby the primary aromatic alcohols are obtained from formaldehyde and the arylhydroxylamines or sodium phenoxides, the following equation representing the reaction: $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{MgCl} + \text{HCHO} = \text{OH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{MgCl} \rightarrow \text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{OMgCl}$. The abnormal behaviour is peculiar to

trioxymethylene, the other aldehydes and ketones giving the normal product; thus magnesium benzyl chloride gives, with paracetaldehyde, benzylmethylcarbinol, $C_6H_5 \cdot CH_2 \cdot CHMe \cdot OH$, and with acetone, benzyl-dimethylcarbinol, $C_6H_5 \cdot CH_2 \cdot CMe_2 \cdot OH$ (Grignard, Abstr., 1900, i, 382).
M. A. W.

Cholesterol. ADOLF WINDAUS (*Ber.*, 1903, 36, 3752).—The compound previously described as hydroxycholestanonol (*Habilitations-schrift, Freiburg*, 1903) and formulated as $C_{27}H_{44}O_3$ is now described as *cholestanonol* and formulated as $C_{27}H_{44}O_2 \cdot H_2O$; it is prepared by reducing with zinc dust and acetic acid a compound, $C_{27}H_{42}O_6N_2$, formed by oxidising cholesterol with fuming nitric acid, the whole of the nitrogen being eliminated in the form of ammonia; cholestanonol crystallises from 75 per cent. alcohol, melts at $142-143^\circ$, and contains a carbonyl and a secondary hydroxyl group. The *formyl* derivative, $C_{28}H_{44}O_3$, crystallises from alcohol in stout needles and melts at $104-105^\circ$. The *acetyl* derivative, $C_{29}H_{46}O_3$, crystallises from alcohol in long prisms and melts at 128° . The *benzoyl* derivative, $C_{34}H_{48}O_3$, crystallises from acetone, melts at 173° , and is very sparingly soluble in alcohol. The *nitrophenylhydrazone*, $C_{33}H_{49}O_3N_3 \cdot C_2H_5 \cdot OH$, separates from alcohol in feathery crystals and melts at 194° .

Cholestanonol is oxidised by chromic acid to *cholestandione*, $C_{27}H_{42}O_3$, a diketone which crystallises from alcohol in needles, melts at 169° , and does not reduce ammoniacal silver nitrate. The *dioxime*, $C_{27}H_{44}O_2N_2$, crystallises from alcohol and melts and decomposes at 205° .

Further oxidation with chromic acid yields a dibasic ketonic acid, $C_{27}H_{42}O_5$, which crystallises from 70 per cent. acetic acid or from benzene, melts (not quite sharply) at $217-219^\circ$, and decomposes at this temperature with liberation of gas. The *magnesium* salt was obtained in minute, felted needles. The *methyl* ester, $C_{29}H_{46}O_5$, crystallises from methyl alcohol and melts at $113-114^\circ$, its *oxime* crystallises from methyl alcohol and melts at 76° . The *anhydride* was prepared, but melted irregularly between 170° and 187° and contained carbon and hydrogen in excess of the amounts required for the formula $C_{29}H_{40}O_4$.
T. M. L.

Cholesterol. VI. JULIUS MAUTHNER and WILHELM SUIDA (*Monatsh.*, 1902, 24, 648—668. See Abstr., 1894, i, 326—486; 1896, i, 425; 1897, i, 31; 1903, i, 625).—In ethereal solution, with nitrogen trioxide, cholesterol forms a derivative, $C_{27}H_{43}O_2N$, which crystallises in white needles, melts at $94-95^\circ$, decomposes slowly at 120° , evolves brown vapours when heated, is stable towards potassium hydroxide, does not form an additive compound with bromine, gives Liebermann's nitroso-reaction and the cholesterol reaction, and yields cholesterol when boiled with alcohol. Cholesteryl acetate and chloride do not react with nitrogen trioxide in ethereal solution.

When treated with nitrous acid, cholesteryl acetate yields *nitrocholesteryl acetate*, $C_{29}H_{45}O_4N$, which crystallises in leaflets or flat needles, melts at $101-102^\circ$, and does not form an additive compound with bromine. On reduction with zinc and glacial acetic acid, nitrocholesteryl acetate yields *cholestanonyl acetate*, $C_{27}H_{43}O_2 \cdot OAc$ (com-

pare Windaus, *Habilitationschrift, Freiburg*, 1903), which crystallises in flat prisms or leaflets, melts at 127° , evolves hydrogen bromide when acted on by bromine in carbon disulphide solution, and forms a *p*-nitrophenylhydrazone, $C_{35}H_{51}O_4N_3$, which crystallises in golden needles and melts at 144° .

Cholestanonol, $C_{27}H_{44}O_2$, obtained on hydrolysis of the acetate, crystallises in delicate, glistening needles, melts at 140° , and yields a *p*-nitrophenylhydrazone, $C_{33}H_{49}O_3N_3$, which crystallises in golden needles and melts at 195° .

Cholestanonol probably contains the grouping $\cdot CO \cdot CH \cdot$ in place of the grouping $\cdot CH \cdot C \cdot$ in cholesterol.

Chlorocholestanone, $C_{27}H_{43}OCl$, formed by reduction of nitrocholesteryl chloride, crystallises in delicate, colourless, glistening needles, and melts at $128.5-129^{\circ}$.

The product obtained on acting with chlorine on a mixture of cholesteryl chloride and half its weight of iodine in chloroform solution is apparently a mixture of two compounds, $C_{27}H_{35}Cl_{11}$ and $C_{27}H_{34}Cl_{12}$. Half of the chlorine is removed on treatment with alcoholic sodium hydroxide, and reduction of the resulting substance with zinc dust and glacial acetic acid leads to a substance containing 4 chlorine atoms.

The action of chlorine on the hydrocarbon, $C_{19}H_{28}$ (see Abstr., 1896, i, 426), in the presence of iodine leads to the formation of a mixture of chlorinated products. The part soluble in ether forms long, colourless needles and melts at $213-214^{\circ}$. Oily products, obtained on distillation of the chloro-compounds with lime, boil between 60° and 235° and give aldehyde reactions. The fractions boiling between 150° and 235° lose hydrogen chloride on distillation under the ordinary pressure.

When heated over a free flame, cholesteryl chloride yields cholesterylene, a hydrocarbon $C_{19}H_{28}$, and hydrocarbons C_8H_{16} (?) and C_8H_{18} (?). When the chloride is heated in a bath, there is also formed a hydrocarbon, $C_{20}H_{28}$ (?), which boils at $241-265^{\circ}$ under 42 mm., and a hydrocarbon, $C_{23}H_{34}$ (?), which boils at $270-286^{\circ}$ under 37-40 mm. pressure.

Cholesterol and oxalic acid in ethereal solution form *cholesterol oxalate*, $(C_{27}H_{44}O)_2 \cdot C_2H_2O_4$, which crystallises in flat needles, sinters at 172° , and melts at 200° .

Cholesteryl oxalate, $(C_{27}H_{43})_2C_2O_4$, formed by heating cholesterol and oxalic acid together at $195-200^{\circ}$, crystallises in colourless, matted needles, sinters at 215° , melts at 224° , and decomposes at 240° .

Cholesterylene is formed by the distillation of cholesteryl chloride with lime or by heating cholesteryl chloride with quinoline.

G. Y.

Preparation of Anthranilic Acid and *N*-Alkylated Anthranilic Acids. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 145604).—The replacement of the chlorine atom of *o*-chlorobenzoic acid in presence of metallic copper or copper salts (compare Abstr., 1903, i, 754) also takes place readily with ammonia or alkylamines. Ammonia at 125° under pressure forms anthranilic acid, together with the sparingly soluble *diphenylamine-2:2'-dicarboxylic acid*. *Ethyl-*

anthranilic acid, $\text{NH}_2\text{Et}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, from ethylamine, crystallises from dilute alcohol in colourless prisms melting at $152\text{--}153^\circ$.

C. H. D.

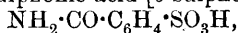
Sulphonic Acids of Phenyl- and Naphthyl-anthranilic Acids. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 146102. Compare preceding abstract).—*o*-Chlorobenzoic acid reacts readily with sulphonic acids of the benzene or naphthalene series on heating the alkali salts in presence of copper or copper salts. Thus, sulphanic acid forms 4'-sulphodiphenylamine-2-carboxylic acid, the *sodium hydrogen* salt of which forms white leaflets decomposing at $265\text{--}266^\circ$ when heated rapidly. The *barium* salt of 3'-sulphodiphenylamine-2-carboxylic acid, from metanilic acid, contains water of crystallisation, which is only slowly lost on heating. The *sodium hydrogen* salt of 3'-sulpho-*p*-tolylamino-2-benzoic acid, from *p*-toluidine-2-sulphonic acid, is sparingly soluble in water and is not completely fused at 280° ; the corresponding salt of 4'-sulpho-*o*-tolylamino-2-benzoic acid, from *o*-toluidine-5-sulphonic acid, melts and decomposes at $265\text{--}266^\circ$.

Similar salts, prepared from a number of aminosulphonic acids of the benzene and naphthalene series, are described.

C. H. D.

***o*-Sulphaminebenzoic and *o*-Carbaminebenzenesulphonic Acids.** FRANCIS DANIEL WILSON (*Amer. Chem. J.*, 1903, 30, 353—373).—By the action of sodium hydroxide on benzoicsulphinide, a nearly quantitative yield of *o*-sulphaminebenzoic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$, is obtained. This acid crystallises in plates or needles and is soluble in alcohol or water; when heated slowly, it melts at 152° , but if heated rapidly melts at 159° . If heated in a tube in a current of dry air, it decomposes at 128° with formation of benzoicsulphinide. The salts of *o*-sulphaminebenzoic acid form well-defined crystals, and, with the exception of the mono-silver, potassium, and ammonium salts, all contain water of crystallisation; when heated, they decompose with formation of benzoicsulphinide at a few degrees above the temperature at which they give off their water of crystallisation. The *sodium*, *potassium*, *calcium*, *barium*, *strontium*, *zinc*, *magnesium*, *copper*, *ammonium*, and *mono-* and *di-silver* salts are described. When the acid is heated with phosphorus oxychloride, it is completely converted into benzoicsulphinide. The *amide*, $\text{NH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$, melts at 263° .

o-Carbaminebenzenesulphonic acid [*o*-sulphobenamide],



obtained by treating the potassium hydrogen salt of *o*-sulphobenzoic acid with ammonium thiocyanate, crystallises from water in large, transparent crystals, is soluble in alcohol, melts at $193\text{--}194^\circ$ (uncorr.), and decomposes when heated at 125° . The *potassium*, *mono-* and *tri-silver*, *sodium*, *barium*, *strontium*, *calcium*, *zinc*, *magnesium*, *copper*, and *ammonium* salts were prepared and analysed. The *chloride*, $\text{NH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$, obtained by heating the potassium salt with phosphorus oxychloride at 100° for half an hour, crystallises in thick, opaque plates, and melts at 63° . If the mixture of the potassium salt and phosphorus oxychloride is merely warmed, potassium

o cyanobenzenesulphonate is produced. When the chloride is treated with a solution of ammonium hydroxide, a white *substance* is formed, which crystallises in opaque plates and does not melt when heated to the boiling point of sulphuric acid. E. G.

Action of Phenols and Alcohols on the Chlorides of *p*-Nitro-*o*-sulphobenzoic Acid. VICTOR JOHN CHAMBERS (*Amer. Chem. J.*, 1903, 30, 373—392).—The observation of Henderson (*Abstr.*, 1901, i, 208), that by the action of phenol on the symmetrical chloride of *p*-nitro-*o*-sulphobenzoic acid the diphenyl ester is produced, is now confirmed. When the unsymmetrical chloride is heated with phenol, the sulphonic chloride of phenyl *p*-nitrobenzoate is formed, but no diphenyl ester is obtained.

The *sulphonic chloride* of phenyl-*p*-nitrobenzoate,
 $\text{CO}_2\text{Ph} \cdot \text{C}_6\text{H}_5(\text{NO}_2) \cdot \text{SO}_2\text{Cl}$,
 crystallises in light brown needles and melts at 145—147°. When this substance is treated with dilute hydrochloric acid, *p*-nitro-*o*-sulphobenzoic acid is produced, whilst if it is boiled with water both the free acid and the monophenyl ester are obtained. By the action of barium hydroxide, the chloride is converted into barium *p*-nitro-*o*-sulphobenzoate and the diphenyl ester. When treated with ammonia, it yields *p*-nitrobenzoicsulphinide and the diphenyl ester, whilst with aniline the anil is produced. By the action of alcohols, the chloride is converted into the monophenyl ester. Barium phenyl *p*-nitro-*o*-sulphobenzoate and the corresponding potassium salt are described.

When alcoholic potassium hydroxide is added slowly to an alcoholic solution of the symmetrical chloride and *o*-cresol, a *substance* is obtained which crystallises in needles, melts at 90°, and is probably di-*o*-tolyl *p*-nitro-*o*-sulphobenzoate. By the action of *o*-cresol on the unsymmetrical chloride, the *o*-sulphonic chloride of *o*-tolyl *p*-nitrobenzoate, $\text{CO}_2(\text{C}_7\text{H}_7) \cdot \text{C}_6\text{H}_5(\text{NO}_2) \cdot \text{SO}_2\text{Cl}$, is produced, which crystallises in white plates and melts at 150°.

If a mixture of the symmetrical chloride and *p*-cresol is treated with dilute potassium hydroxide, di-*p*-tolyl *p*-nitro-*o*-sulphobenzoate is produced, which melts at 118°. By the action of *p*-cresol on the unsymmetrical chloride, the *o*-sulphonic chloride of *p*-tolyl *p*-nitrobenzoate is obtained, which crystallises in small needles or prisms and melts at 152° (uncorr.).

o-Nitrophenol reacts with each chloride to form di-*o*-nitrophenyl *p*-nitro-*o*-sulphobenzoate, which crystallises in slender needles and melts at 164°.

p-Nitrophenol reacts with both chlorides in a similar manner with the production of the di-*p*-nitrophenyl ester, which crystallises in thick needles and melts at 152°.

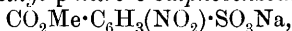
Resorcinol and quinol react with both chlorides, but no definite product was isolated.

Di- β -naphthyl *p*-nitro-*o*-sulphobenzoate, obtained by the action of β -naphthol on the unsymmetrical chloride, crystallises in white needles and melts at 134°.

p-Aminophenol reacts with the unsymmetrical chloride, but no definite product could be isolated.

By the action of phenol on the symmetrical chloride in the presence of ammonia, diphenyl *p*-nitro-*o*-sulphobenzoate is produced together with phenyl *p*-nitro-*o*-sulphaminebenzoate, $\text{CO}_2\text{Ph}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{SO}_2\cdot\text{NH}_2$, which crystallises in prisms and melts at 135° , and by the action of dilute alkali or water is converted into *p*-nitrobenzoic sulphinide. When the unsymmetrical chloride is treated in the same way, phenyl *p*-nitro-*o*-sulphaminebenzoate is not obtained.

It has been shown by Henderson (*loc. cit.*) that the symmetrical chloride reacts with alcohols with the formation of alkyl esters. When the unsymmetrical chloride is treated with methyl alcohol, the sulphonic chloride of methyl *p*-nitrobenzoate, $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{SO}_2\text{Cl}$, is produced, which crystallises in small, thick prisms, melts at 82° , and when boiled with alcohol is converted into methyl *p*-nitro-*o*-sulphobenzoate. Sodium methyl *p*-nitro-*o*-sulphobenzoate,



crystallises in transparent plates; the corresponding potassium salt was prepared.

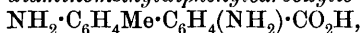
The sulphonic chloride of ethyl *p*-nitrobenzoate crystallises in white needles, melts at 68° , and when boiled with alcohol is converted into ethyl *p*-nitro-*o*-sulphobenzoate. Barium ethyl *p*-nitro-*o*-sulphobenzoate and the corresponding potassium salt were prepared and analysed.

The sulphonic chloride of propyl *p*-nitrobenzoate forms large, thin plates, melts at 76° , and is converted by boiling alcohol into propyl *p*-nitro-*o*-sulphobenzoate. Barium propyl *p*-nitro-*o*-sulphobenzoate and the corresponding potassium salt were prepared and analysed. E. G.

trans-Phenyltrimethylenecarboxylic Acid. EDUARD BUCHNER and JOSEF GERONIMUS (*Ber.*, 1903, 36, 3782—3786).—Ethyl *trans*-2-phenyltrimethylenecarboxylate, $\text{C}_6\text{H}_5\cdot\text{C}_3\text{H}_4\cdot\text{CO}_2\text{Et}$, prepared by heating styrene with ethyl diazoacetate at 100° during 12—15 hours, boils at $144\text{—}148^\circ$ under 15 mm. pressure, crystallises from light petroleum in long, colourless needles, and melts at 39° . The acid separates from hot water in silky needles, melts at 105° , and is not altered by permanganate. The amide crystallises from hot water in colourless, glistening flakes and melts at $187\text{—}188^\circ$. The calcium salt, $(\text{C}_{10}\text{H}_9\text{O}_2)_2\text{Ca}\cdot 2\text{H}_2\text{O}$, was crystallised from water, dried, and distilled; no phenyltrimethylene was produced, but styrene and allylbenzene were detected in the distillate. Nitrophenyltrimethylenecarboxylic acid, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_3\text{H}_4\cdot\text{CO}_2\text{H}$, crystallises from water and melts at 154° . The amino-compound was not analysed; its hydrochloride separates from alcohol in yellow needles and melts (not sharply) at $173\text{—}185^\circ$; the amino-acid is oxidised by permanganate to *trans*-1:2-trimethylenedicarboxylic acid. T. M. L.

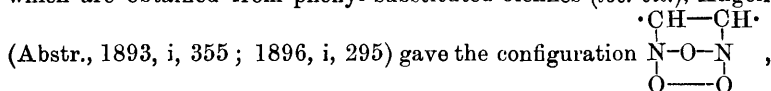
Diaminomethyldiphenylcarboxylic Acid. CHEMISCHE FABRIK VORM. WEILER-TER-MEER (D.R.-P. 145063).—When *o*-nitrotoluene is reduced by heating with iron or zinc and sodium hydroxide solution at 100° , *o*-azoxytoluene is precipitated on dilution, and on addition of acids toluene-*o*-azobenzoic acid separates, crystallising from toluene in orange-red needles with blue lustre, and melting at about 148° . On warming with sodium hydroxide and zinc dust until decolorised, further reduction to toluene-*o*-hydrazobenzoic acid, melting at about 136° ,

takes place. On warming with strong hydrochloric acid and adding sodium hydroxide, *diaminomethyldiphenylcarboxylic acid*,



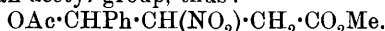
is precipitated as an oil, rapidly solidifying, and crystallising from water or dilute alcohol in slender, white needles which melt and evolve carbon dioxide at 183° . It forms easily soluble salts with acids and sparingly soluble salts with bases. The *sodium* salt forms small needles, of which 8.7 parts dissolve in 100 parts of water at 20° . The *barium* salt crystallises in leaflets, of which 2.5 parts dissolve in 100 parts of water at 20° . C. H. D.

Pseudonitrosites. HEINRICH WIELAND (*Annalen*, 1903, 329, 225—268. Compare Abstr., 1903, i, 764).—To the pseudonitrosites which are obtained from phenyl-substituted olefines (*loc. cit.*), Angeli

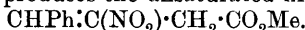


but on account of the various reactions detailed later, it is thought that these substances are best represented as dimolecular compounds of the form $\text{NO}_2 \cdot \text{CH} : \text{CH} \cdot (\text{N}_2\text{O}_2) \cdot \text{CH} : \text{CH} \cdot \text{NO}_2$. When boiled with alcohol, the pseudonitrosites are converted into "nitro-oximes," thus the derivative of methyl phenylisocrotonate yields the oxime of methyl benzoylnitropropionate, $\text{OH} \cdot \text{N} : \text{CPh} \cdot \text{CH}(\text{NO}_2) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$; the nitro-oximes are relatively stable, and are hydrolysed to hydroxylamine and nitro-ketones (compare Abstr., 1903, i, 836, 837).

Acetic anhydride brings about the same decomposition, but in the presence of a few drops of sulphuric acid the oxime group is eliminated and replaced by an acetyl group, thus:



Sulphuric acid alone produces the unsaturated nitro-ester,



By alkali hydroxides in the presence of alcohols, the pseudonitrosites are decomposed into hyponitrite and the alkali salt of the ether, $\cdot \text{CH}(\text{OMe}) \cdot \text{CMe} : \text{NO}_2\text{K}$, which, on acidifying, is decomposed into methyl alcohol and a β -nitropropylene derivative, $\cdot \text{CH} : \text{C}(\text{NO}_2) \cdot \text{CH}_3$; when the pseudonitrosites are heated with alkali hydroxides, nitroethane and an aromatic aldehyde are formed.

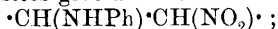
Aromatic bases give anilino-nitro-derivatives, thus from the nitrosite of methyl phenylisocrotonate, methyl β -nitro- γ -anilino- γ -phenylbutyrate, $\text{NHPh} \cdot \text{CHPh} \cdot \text{CH}(\text{NO}_2) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$, is formed.

The pseudonitrosites are converted, under certain conditions, into glyoxime peroxides, $\begin{array}{c} \cdot \text{C} - \text{C} \cdot \\ | \quad | \\ \text{N} \cdot \text{O} \cdot \text{O} \cdot \text{N} \end{array}$; these substances are, however, most

readily formed when the nitro-oximes, the decomposition products of the pseudonitrosites, are set free from their salts. It is supposed that the salts of the nitro-oximes are nitronates, and that the free nitronic acid, $\begin{array}{c} \cdot \text{C} - \text{C} \text{Me} \\ | \quad | \\ \text{N} \cdot \text{OH} \quad \text{HO} \cdot \text{N} \end{array}$, loses water, changing into the peroxide.

A comparison of the behaviour of the nitrosites and the pseudo-

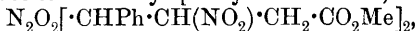
nitrosites has led to the view that these two classes of substances differ in that the nitrosites are nitrites, whilst the pseudo-compounds are nitro-derivatives, thus, amylene nitrosite is represented by the formula $N_2O_2(CHMe \cdot CMe_2 \cdot ONO)_2$, and anetholpseudonitrosite by the formula $[OMe \cdot C_6H_4 \cdot CH_2 \cdot CH(CH_2 \cdot NO_2)]_2 N_2O_2$. Thus the nitrosites, with aniline, yield the anilino-oximes, $\cdot C(:NOH) \cdot CH(NHPh) \cdot$, whilst the pseudonitrosites give anilino-nitro-compounds,



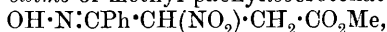
with potassium methoxide, the nitrosites give compounds of the type $\cdot C(:NOK) \cdot CH(OMe) \cdot$, and the pseudonitrosites $\cdot CH(OMe) \cdot C(:NO_2K) \cdot$.

The constitution of the bisnitroso-group is discussed (compare Piloty, Abstr., 1902, i, 734), and Thiele's theory of "partial" valency is introduced in order to explain the unstable dimolecular nitroso-compounds.

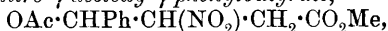
The *pseudonitrosite* of methyl phenylisocrotonate,



is prepared by leading nitrous fumes (from white arsenic and nitric acid) into an ethereal solution of the ester, when a white, crystalline powder is precipitated; it is purified by washing with ether, and then melts and decomposes at 118° ; it is changed by all solvents except chloroform. Phenol and sulphuric acid give a dark blue coloration, which becomes bordeaux-red on dilution; it dissolves in alcoholic alkali with evolution of nitrous oxide and formation of a yellow solution; concentrated sulphuric acid causes the evolution of nitrous oxide. The *nitro-oxime* of methyl phenylisocrotonate,



is prepared from the nitrosite by boiling with alcohol; on adding water, a solid separates which crystallises from benzene in needles melting and decomposing at 128° , and is soluble in alkali hydroxides but not in carbonates; when boiled with acids, hydroxylamine is set free. *Methyl β -nitro- γ -acetoxy- γ -phenylbutyrate*,



is obtained when the pseudonitrosite is treated with acetic anhydride containing a few drops of sulphuric acid, and forms large, prismatic crystals melting at 89° . *Methyl β -nitro- γ -anilino- γ -phenylbutyrate*, $NHPh \cdot CHPh \cdot CH(NO_2) \cdot CH_2 \cdot CO_2Me$, is prepared by heating the pseudonitrosite in alcoholic solution with aniline, forms colourless crystals melting at 122° , and yields a well-crystallised nitrosoamine. With phenylhydrazine, a reaction took place, but of the products, the phenylhydrazone of benzaldehyde was alone isolated.

Ammonium quadroxalate, $C_2O_4H(NH_4) \cdot C_2O_4H_2 \cdot 2H_2O$, separates in large plates from the mother liquors obtained in the preparation of the pseudonitrosite; it melts and decomposes at 128° .

The *pseudonitrosite* of benzylideneacetone,



is obtained in colourless needles by leading nitrous fumes over an ethereal solution of benzylideneacetone; it becomes red at 100° and melts and decomposes at $109-110^\circ$. With phenol and sulphuric acid, it gives a cherry-red coloration which becomes blue when alkali is added. The *nitro-oxime* of benzylideneacetone (the *oxime* of benzoyl-nitroacetone), $OH \cdot N : CPh \cdot CHAc \cdot NO_2$, prepared by saturating a

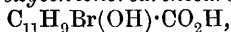
solution of benzylideneacetone in benzene with nitrous fumes, crystallises in slender needles softening at 70° , and melting to a milky liquid at 84° , which becomes clear at 100° . By alcoholic potassium hydroxide it is decomposed into nitroacetophenoxime and acetic acid. When boiled with concentrated aqueous hydrogen chloride, it is converted into *phenylmethylnitroisooxazole*, $\begin{array}{c} \text{C}(\text{NO}_2):\text{CMe} \\ | \\ \text{CPh}:\text{N}-\text{O} \end{array}$, which crystallises in colourless, four-sided pyramids melting at 48° .

The pseudonitrosite of anethole, $(\text{N}_2\text{O}_2)[\text{CH}(\text{C}_6\text{H}_4\cdot\text{OMe})\cdot\text{CHMe}\cdot\text{NO}_2]_2$, prepared by adding sodium nitrite to an acetic acid solution of anethole (compare Tönnies, Abstr., 1881, 167), decomposes at about 120° , and by boiling with alcohol is converted into the corresponding *nitroxime*, which crystallises in needles melting at 87° . The latter is very readily converted into the glyoxime peroxide (m. p. 97°) in the manner described above (compare Tönnies, *loc. cit.*). β -Nitroanethole, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CMe}\cdot\text{NO}_2$, is prepared by adding the pseudonitrosite to an alcoholic solution of ammonia and crystallises in yellow needles melting at 48° . It is soluble in cold alkali hydroxides, but by hot solutions is converted into anisaldehyde. The nitroanethole is also formed by the carefully regulated action of alkali hydroxides on the pseudonitrosite, hyponitrous acid being at the same time produced.

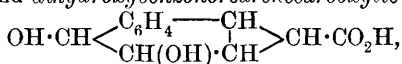
When the anethole is treated in acetic acid solution with sodium nitrite, the temperature being allowed to rise, the glyoxime peroxide is formed together with the *amphi-dioxime* of anisylmethyl-1:2-diketone, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{NOH})\cdot\text{C}(\text{NOH})\cdot\text{CH}_3$, which was isolated as a yellow solid melting and decomposing at 206° . K. J. P. O.

Benzonorcaradienecarboxylic Acid. EDUARD BUCHNER and STEPHAN HEDIGER (*Ber.*, 1903, 36, 3502—3509).—The reaction between ethyl diazoacetate and naphthalene is similar to that between ethyl diazoacetate and benzene (Braren and Buchner, Abstr., 1901, i, 85, 385). The naphthalene is heated at 140 — 145° on an oil-bath, and the ester is added very gradually; nitrogen is steadily evolved, and the product is isolated by fractional distillation under reduced pressure. *Ethyl benzonorcaradienecarboxylate*, $\text{C}_{10}\text{H}_8\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, is a viscid, colourless oil, becoming yellow in the air, boiling at 163 — 164° under 11 mm. pressure, and reducing an alkaline solution of potassium permanganate. It combines with bromine in chloroform solution, forming a *dibromide*, which crystallises from alcohol in colourless needles and melts at 95 — 96° .

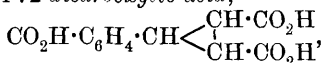
Benzonorcaradienecarboxylic acid, $\begin{array}{c} \text{CH}:\text{CH}:\text{C} \text{---} \text{CH} \\ | \quad | \quad | \\ \text{CH}:\text{CH}:\text{C} \cdot \text{CH}:\text{CH}:\text{CH} \end{array} > \text{CH}\cdot\text{CO}_2\text{H}$, prepared by hydrolysing the ester with sodium ethoxide and decomposing the sodium salt by acid, forms colourless crystals melting at 165 — 166° , insoluble in water, but dissolving readily in alcohol or benzene. The *amide* forms colourless crystals melting at 217° . The *dibromide* melts and decomposes at about 168° , and reacts with boiling water to form *bromohydroxybenzonorcaradienecarboxylic acid*,



crystallising from ether in colourless needles melting and decomposing at 170—173°, and *dihydroxybenzonorcaradienecarboxylic acid*,



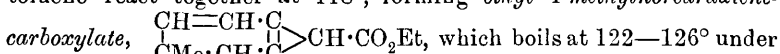
melting at 203°, and forming a faintly yellow *diacetyl* derivative melting at 216°. Potassium permanganate oxidises an alkaline solution of benzonorcaradienecarboxylic acid, one benzene ring of the naphthalene nucleus being broken down, forming *carboxyphenyl trimethylene-trans-1:2-dicarboxylic acid*,



which crystallises in yellowish-white needles melting at about 273—275°. Fuming nitric acid converts this into a *nitro-acid*, separating from dilute alcohol in greenish-yellow crystals decomposing at about 290°. Ferrous hydroxide and ammonia reduce this to the corresponding *amino-acid*, crystallising from water in faintly yellow needles decomposing at 259°, and being oxidised by potassium permanganate to trimethylene-trans-1:2:3-tricarboxylic acid, identical with that prepared by Buchner and Witter (Abstr., 1895, i, 269).

C. H. D.

Ethyl Diazoacetate and Toluene. EDUARD BUCHNER and LEON FELDMANN (*Ber.*, 1903, **36**, 3509—3517).—Ethyl diazoacetate and toluene react together at 118°, forming *ethyl 4-methylnorcaradienecarboxylate*,



which boils at 122—126° under 15 mm. pressure, and reacts with cold aqueous ammonia, on long contact, with the formation of *4-methylnorcaradienecarboxylamide*, crystallising from ether or hot water and melting at 131°. A portion of the original oil remains unattacked, and when hydrolysed by boiling with 30 per cent. sulphuric acid yields *4-methylcycloheptatrienecarboxylic acid*, $\text{C}_7\text{H}_6\text{Me} \cdot \text{CO}_2\text{H}$, crystallising from boiling water in flat needles melting at 107—108°. The *amide* forms long needles melting at 99°. Hydrolysis of the *4-methylnorcaradienecarboxylamide* yields an amorphous compound, together with a small quantity of *p*-tolylacetic acid.

C. H. D.

Preparation of Bromoindigotin. FARBERWERKE VORM. MEISTER, LUCIUS, and BRÜNING (D.R.-P. 144249).—Indigo-white reacts with bromine at the ordinary temperature with development of heat and formation of hydrogen bromide. A bromoindigo-white is first produced, and may be isolated by employing only a small quantity of bromine and extracting with acetone, in which bromoindigo-white is soluble, whereas bromoindigotin remains undissolved. In the presence of an excess of bromine, the intermediate compound is oxidised to bromoindigotin, containing from 1 to 2 atoms of bromine in the molecule.

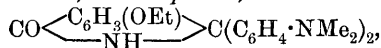
Bromoindigotin is a violet-blue powder and dissolves in concentrated sulphuric acid to a yellowish-green solution, slowly becoming

blue. In its behaviour towards organic solvents it resembles indigotin, but the solution in hot nitrobenzene, unlike that of indigotin, is not fluorescent. The shade produced in dyeing is more violet than that of indigotin. C. H. D.

Triphenylmethane Derivatives and their Oxidation Products, obtained from Tetramethyldiaminobenzhydrol and *m*-Ethoxybenzoic Acid, and its Amide, Methylamide, and Dimethylamide. PAUL FRITSCH (*Annalen*, 1903, 329, 66—81. Compare Abstr., 1897, i, 72).—*m*-Ethoxybenzamide, $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH}_2$, prepared by heating together an intimate mixture of *m*-ethoxybenzoic chloride and ammonium carbonate, crystallises in needles melting at $139\text{--}139.5^\circ$. The corresponding methylamide is prepared by shaking a benzene solution of the acid chloride with a 33 per cent. solution of methylamine; it crystallises in needles melting at 64° . The dimethylamide is prepared in a similar manner and was only obtained as an oil.

The triphenylmethane derivatives were prepared by dissolving an intimate mixture of the acid or one of the foregoing amides and benzhydrol in 90 per cent. sulphuric acid, pouring the mixture on to ice after the benzhydrol had disappeared and neutralising the acid, when a mixture of isomeric bases was precipitated; from this, however, only one base could be isolated in small quantity; in this base, the condensation had taken place in the para-position to the ethoxy-group. Tetramethyldiamino-*m*-ethoxytriphenylmethane-*o*-carboxylic acid, $\text{CH}(\text{C}_6\text{H}_3 \cdot \text{NMe}_2)_2 \cdot \text{C}_6\text{H}_3(\text{OEt}) \cdot \text{CO}_2\text{H}$, is extracted from the mixture of bases by means of carbon disulphide, and crystallises from benzene in needles melting at $197\text{--}198^\circ$, and when quite free from the isomeric bases gives no coloration with chloranil. The corresponding amide, prepared by using *m*-ethoxybenzamide, crystallises in concentric groups of needles melting at $191\text{--}192^\circ$. The methylamide, prepared in a similar manner, crystallises in flattened prisms or needles melting at $185\text{--}186^\circ$. The dimethylamide forms quadratic crystals melting at $139\text{--}140^\circ$.

These triphenylmethane derivatives were oxidised by adding lead dioxide (1 mol.) to a very dilute ice-cold solution of the base (1 mol.) in hydrochloric acid (4 mols.); after half an hour, the lead was precipitated by sodium sulphate. From the carboxylic acid above mentioned, the *phthalein*, $\text{CO} \langle \text{C}_6\text{H}_3(\text{OEt}) \rangle \text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$, was obtained by neutralising the acid mother liquor from which the lead had been precipitated, and crystallised from a mixture of carbon disulphide and petroleum in pale yellow, six-sided plates melting at $167\text{--}168^\circ$; it dissolves in acetic acid with a pale green coloration, rapidly becoming more intense on heating. When boiled with zinc dust and acetic acid, it is reconverted into the leuco-compound. From the carboxylamide, the compound,



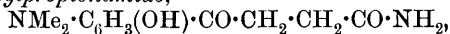
is obtained and crystallises in lustrous leaflets, rhombic plates, or long needles melting at $242\text{--}244^\circ$, which dissolves in acids with a deep

green coloration, and is not reduced by zinc dust and acetic acid. The corresponding *methylimide* is prepared in a similar manner and crystallises in prismatic leaflets melting at 181° ; it cannot be reduced by zinc and acetic acid. From the corresponding dimethylamide, the compound, $\text{OEt}\cdot\text{C}_6\text{H}_3(\text{CO}\cdot\text{NMe}_2)\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{OH}$, is obtained, and crystallises in rhombohedra melting at 188° ; this dye colours wool a brilliant green.

In order to determine the constitution of these substances, the foregoing carboxylic acid was distilled with many times its weight of baryta in a stream of hydrogen, when the base, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, was obtained and crystallised in colourless needles melting at 125° . The same base was also prepared by condensing *p*-ethoxybenzaldehyde with dimethylaniline in the presence of zinc chloride.

K. J. P. O.

β -4-Dimethylamino-2-hydroxybenzoylpropionic Acid and its Application in Preparing Succinein Dyes. ARTHUR WEINSCHENK (*Zeit. Farb. Text. Chem.*, 1903, 2, 409—413).— *β -4-Dimethylamino-2-hydroxybenzoylpropionamide*,



prepared by heating succinimide with *m*-dimethylaminophenol and boric acid at 150 — 175° , crystallises from pyridine in needles and melts and partially decomposes at 217 — 220° . On hydrolysis with alkali, it readily gives *β -4-dimethylamino-2-hydroxybenzoylpropionic acid*, which is a crystalline powder melting at 190° ; when heated with resorcinol and concentrated sulphuric acid for $2\frac{1}{2}$ hours at 150 — 160° , it gives a *succinoresorcinorhodol*, whilst from pyrogallol under similar conditions a *succinopyrogallorhodol* is obtained. Both of these dyes yield crystalline salts; the colours they give are not fast to soap.

W. A. D.

Esterification of *ortho*-Aldehydo-acids. RUDOLF WEGSCHEIDER, LEO KUŠY VON DÚBRÁV and PETER VON RUŠNOV (*Monatsh.*, 1903, 24, 790—804. Compare Abstr., 1902, i, 619; 1903, i, 562).—Nitro-opianic acid is found to melt at $168\cdot5$ — $169\cdot5^{\circ}$. Of the two methyl esters, that which is obtained by the action of methyl iodide on the silver salt and melts at 76 — 78° is the true ester. Fink's ester (*Ber.*, 1898, 31, 924), which is obtained on heating the acid with methyl alcohol, crystallises in white needles, melts at $181\cdot5$ — $182\cdot5^{\circ}$, and is the *ψ -methyl ester*. Both methyl esters are only slightly hydrolysed by boiling water; when boiled with alcoholic potassium hydroxide, the *ψ -methyl ester* yields a *product* which forms yellow crystals, melts and decomposes at 260° , and is also obtained on boiling nitro-opianic acid with alcoholic potassium hydroxide.

Oxidation of the methyl ester with potassium permanganate in aqueous methyl alcoholic solution leads to the formation of nitro-hemipinic acid and not of methyl hydrogen nitrohemipinate. Potassium permanganate has no action on the *ψ -methyl ester* in acetone or aqueous methyl alcoholic solution; a portion of the *ψ -ester* is hydrolysed by the water.

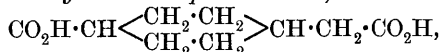
The formation of a second ethyl ester of nitro-opianic acid has not yet been accomplished (compare Prinz, Abstr., 1882, 402). G. Y.

Derivatives of Taurine and Synthesis of Taurocholic Acid. SIEGFRIED TAUBER (*Beitr. chem. Physiol. Path.*, 1903, 4, 323—330).—Finely divided taurine reacts with benzoic anhydride at 250° yielding a compound, $C_{15}H_{20}ON_2S_2$, probably according to the equation $C_{14}H_{10}O_3 + 2C_2H_5O_3NS = C_{15}H_{20}ON_2S_2 + 3CO_2 + 2H_2O$. The compound is precipitated from its alcoholic solution by the addition of acetone, melts at 175°, and is readily soluble in alcohol, ether, or hot light petroleum. Taurine and phthalic anhydride yield a compound, $C_{25}H_{20}O_{16}N_3S_2 \cdot 7H_2O$, which crystallises from acetone in long, thin, hexagonal plates, melts at 50°, and is readily soluble in water.

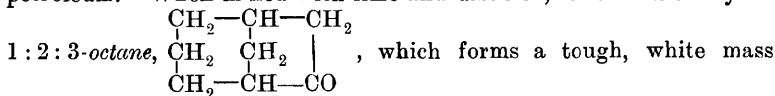
Unlike the majority of amino-fatty acids, taurine cannot be converted into its esters by Curtius's method. Phenylcarbimide does not combine with taurine, and it has been found impossible to introduce acyl groups into the taurine molecule.

Taurine and sodium cholate react at 265° yielding a product which appears to be identical with sodium taurocholate. J. J. S.

Synthesis of a Dicyclic Ring-compound. GUSTAV KOMPPA and TAVI HIRN (*Ber.*, 1903, 36, 3610—3612).—Homöisophthalic acid, prepared by hydrolysing *m*-cyanobenzyl cyanide (Reinglass, Abstr., 1891, i, 1344) with sulphuric acid, crystallises from water in flat, radiating groups of needles or broad tablets, melting at 184—185°, and is readily soluble in alcohol, sparingly in ether, almost insoluble in benzene or chloroform (compare Allen and Underwood, Abstr., 1884, 587). Sodium amalgam reduces it to a tetrahydro-acid, which, by the addition of hydrogen bromide and further reduction with sodium amalgam, is converted into *hexahydrohomöisophthalic acid*,



which crystallises from water in small, thick needles melting at 158°, but sintering at a much lower temperature when slowly heated, dissolving readily in acetone, sparingly in water, benzene, or light petroleum. When mixed with lime and distilled, it forms *ketodicyclo-*



smelling like camphor and melting at 157—158°. The *semicarbazone* crystallises in microscopic needles melting at 189—190°, and dissolves readily in methyl or ethyl alcohol, sparingly in water, ether, or benzene.

C. H. D.

Constitution of Derivatives of Santonin. EDGAR WEDEKIND (*Ber.*, 1903, 36, 3461—3464).—Controversial, in reply to Francesconi (Abstr., 1903, i, 830). T. M. L.

Action of Light and of Alkalis on Santonin and its Derivatives. Photosantoninic Acid. LUIGI FRANCESCONI and G. MAGGI (*Gazzetta*, 1903, 33, ii, 65—80).—On exposing a solution of santonin

(1 mol.) in normal potassium hydroxide solution (3 mols.) to sunlight for two months, it was found to yield a compound, $C_{30}H_{42}O_9$, identical with that described by Sestini (Abstr., 1877, i, 471), to which the authors give the name photosantoninic acid; it separates from acetic acid in crystals, softens at 200° , begins to colour at 230° , melts at $258-260^\circ$, and it has $[\alpha]_D -9.88^\circ$. Its *barium* and *silver* salts were prepared, and also its *diethyl* ester, which separates from light petroleum or aqueous alcohol in white crystals melting at 132° . The action of acetic anhydride on the acid yields the *acetyl* derivative of the dilactone of photosantoninic acid, $C_{32}H_{40}O_8$, which forms white, acicular crystals melting at $199-201^\circ$.

From the results of these and previous researches, the authors draw the following conclusions: (1) the action of hydrochloric acid on santonin yields desmotroposantonin, whilst under the influence of light a resinous substance, soluble in sodium carbonate, is also formed. (2) Santonic acid is not acted on by hydrochloric acid and light. (3) Potassium hydroxide and light have no action on santonic or photosantoninic acid, whilst with *isophotosantoninic* acid alone, or mixed with photosantoninic acid, the former, which is an aldehydo-acid, is attacked. (4) Santonin is converted by potassium hydroxide, in the light, into photosantoninic and photosantoninic acids, the proportion of the latter formed increasing with the amount of alkali employed. A tabular *résumé* of the behaviour of santonin and its derivatives towards potassium hydroxide in the dark and in the light and towards hydrochloric acid is given.

The chemical actions of light are classified by the authors under the following headings:—(1) Stereoisomeric transformation. (2) Polymerisation. (3) Intermolecular reactions. (4) Reciprocal actions and photosynthesis. (5) Isomerisation by the displacement of ethylene linkings. Examples of these different actions are quoted.

The formation of photosantoninic acid is assumed to be due to the reciprocal action of santonic acid and nascent photosantoninic acid, but the mode of combination is as yet unknown. T. H. P.

Identity of Stenhouse's Larixinic Acid and Maltol. ALBERTO PERATONER and A. TAMBURELLO (*Ber.*, 1903, 36, 3407—3409).—The compound obtained by Stenhouse (this Journal, 1863, 16, 310) from the bark of larches, and described as larixinic acid, $C_{10}H_{10}O_5$, is now shown to be identical with Brand's (Abstr., 1894, i, 270) and Kiliani's (*ibid.*, 1895, i, 164) maltol. It melts at 159° and yields a benzoyl derivative melting at 115° . J. J. S.

Hexahydrobenzaldehyde, Hexahydroacetophenone, and the corresponding Secondary Alcohol. LOUIS BOUVEAULT (*Bull. Soc. chim.*, 1903, [iii], 29, 1049—1051. Compare Bouveault and Blanc, Abstr., 1903, i, 673).—*Hexahydrobenzaldehyde*, $C_6H_{11}CHO$, obtained by oxidation of the corresponding alcohol (*loc. cit.*), is a colourless liquid with a suffocating odour, recalling simultaneously that of benzaldehyde and of valeraldehyde; it boils at 159° and has a sp. gr. 0.945 at $0/4^\circ$. The *sodium bisulphite* compound is crystalline and somewhat soluble in water. The *semicarbazone* is crystalline, melts at

176°, is readily soluble in alcohol, less so in water, and insoluble in ether or benzene.

cycloHexylmethylcarbinol, $C_6H_{11} \cdot CHMe \cdot OH$, obtained by the action of acetaldehyde on the magnesium derivative of chlorocyclohexane, is a viscous liquid with a slight odour of peppermint; it boils at 87° under 11 mm. pressure, and has a sp. gr. 0.942 at 0°/4°. It is oxidised by chromic acid in presence of sulphuric acid to *hexahydroacetophenone*, $C_6H_{11} \cdot COMe$, a colourless liquid with a pleasant odour resembling that of the aliphatic ketones of similar molecular weight; it boils at 68° under 12 mm. pressure, and has a sp. gr. 0.937 at 0°/4°. The *sodium bisulphite* compound is crystalline, and the *semicarbazone* forms fine, white lamellæ, melts at 175°, is slightly soluble in boiling water, readily so in alcohol, and insoluble in ether, benzene, or light petroleum. T. A. H.

p-Halogen-*o*-nitrobenzaldehydes. FRANZ SACHS and RICHARD KEMPF (*Ber.*, 1903, 36, 3299—3303).—When 2-nitro-4-aminobenzaldoxime is distilled with aqueous ferric chloride, a 60 per cent. yield of 4-chloro-2-nitrobenzaldehyde is obtained; this crystallises from dilute alcohol in long, yellowish, silky needles, melts at 67°, and can also be obtained from 2-nitro-4-aminobenzaldoxime by means of the diazo-reaction. The *phenylhydrazone*, $NO_2 \cdot C_6H_3Cl \cdot CH : N_2HPh$, separates from alcohol as a dark reddish-brown, crystalline powder and melts at 180—181° (corr.). The *semicarbazone*, $C_8H_7O_3N_4Cl$, crystallises from glacial acetic acid in small, bright yellow, rectangular plates and melts at 269—270° (uncorr.). 4-Chloro-2-nitrosobenzoic acid, obtained by exposing the aldehyde dissolved in benzene to light, crystallises from dilute alcohol in small, white rhombohedra.

4-Bromo-2-nitrobenzaldehyde, obtained by diazotising 2-nitro-4-aminobenzaldoxime dissolved in hydrobromic acid and decomposing the product with copper powder, crystallises from alcohol and melts at 97—98° (corr.); the *phenylhydrazone* forms lustrous, brownish-red needles and melts at 181—182° (corr.).

4-Iodo-2-nitrobenzaldehyde melts at 110—111° and its *phenylhydrazone* at 185° (corr.). W. A. D.

Reaction of Ethyl α -Cyanopropionate with Benzaldehyde. LODOVICO BECCARI (*Atti R. Accad. Torino*, 1903, 38, 547—555).—The action of ethyl α -cyanopropionate (2 mols.) on benzaldehyde (1 mol.) in presence of ammonia (2 mols.) yields: (1) a small quantity of a compound, $C_{18}H_{17}ON_3$, separating from alcohol as a heavy, crystalline powder which melts and decomposes at 210°; (2) α -cyanopropionamide, which melts at 105—106°, and not at 85° as was stated by Henry (*Bull. Acad. Roy. Belg.*, 1889, 680); (3) a compound, $C_{18}H_{17}ON_3$, to which the constitution $CHPh : N \cdot CHPh \cdot CMe(CN) \cdot CO \cdot NH_2$, is ascribed; it is a neutral, unstable compound separating from alcohol in white, acicular crystals melting and decomposing at 198°, and is soluble to a slight extent in chloroform, ether, or benzene; with alkalis or dilute acids, it yields benzaldehyde and ammonia, the amount of the latter corresponding with two-thirds of the total nitrogen present. It is also obtained by the action (1) of benz-

aldehyde (2 mols.) on α -cyanopropionamide (1 mol.) in presence of aqueous or, better, alcoholic ammonia and (2) of α -cyanopropionamide (1 mol.) or hydrobenzamide (1 mol.) in alcoholic solution. The ester, $\text{CHPh}\cdot\text{N}\cdot\text{CHPh}\cdot\text{CMe}(\text{CN})\cdot\text{CO}_2\text{Et}$, corresponding with the above amide, is obtained by the interaction of ethyl α -cyanopropionate and hydrobenzamide, and separates from alcohol in crystals which melt and decompose at 195° and are insoluble in water. T. H. P.

o-Tolualdehyde. H. FOURNIER (*Compt. rend.*, 1903, 137, 716—717).—Potassium dichromate and sulphuric acid oxidise *o*-tolylcarbinol, prepared by Tiffeneau and Delange's method (this vol., i, 48), to *o*-tolualdehyde, boiling at 90° (corr.) under 20 mm. pressure and at 197° under the ordinary pressure. The semicarbazide melts at 209° , and the semicarbazide of *p*-tolualdehyde at 215° . Phenylbenzylhydrazine has certain advantages over semicarbazide for the characterisation of aromatic aldehydes, and forms very stable crystalline derivatives. The following were prepared:

| | M.p. |
|--|-------------|
| <i>o</i> -Tolualdehydephenylbenzylhydrazone | 87° |
| <i>p</i> -Tolualdehydephenylbenzylhydrazone | 140° |
| Phenylacetaldehydephenylbenzylhydrazone | 83° |
| <i>p</i> -Ethylbenzaldehydephenylbenzylhydrazone | 104° |

C. H. D.

Nitrovanillin. F. HAYDUCK (*Ber.*, 1903, 36, 3528).—The *m*-nitrovanillin and *o*-nitroprotocatechuic aldehyde described by the author (*Abstr.*, 1903, i, 826) as new substances have already been prepared by Vogl (*Abstr.*, 1899, i, 697) and by Pschorr and Sumuleanu (*Abstr.*, 1900, i, 178) respectively. W. A. D.

The Migration of Phenyl. MARC TIFFENEAU (*Compt. rend.*, 1903, 137, 989—991. Compare *Abstr.*, 1902, i, 666).—The compound obtained by the action of magnesium phenyl bromide on chloroacetone is decomposed by gentle heat, forming benzyl methyl ketone, $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}_3$. When the phenyl group is at a distance from the chlorohydrin group in the original compound, no migration of the phenyl takes place, but aldehydes are formed. It is concluded that in the passage from an ethylene oxide to an aldehyde or ketone, phenyl is more mobile than hydrogen, and hydrogen more mobile than alkyl groups. C. H. D.

Condensation of Carbon Tetrachloride with Chlorobenzene by means of the Friedel and Crafts Reaction. JAMES F. NORRIS and W. C. TWIEG (*Amer. Chem. J.*, 1903, 30, 392—399).—It has been shown by Norris and Green (*Abstr.*, 1902, i, 379) that chlorobenzene reacts with carbon tetrachloride in presence of aluminium chloride with the formation of a dichlorobenzophenone chloride. It is now found that the product consists of a mixture of the chlorides of 4:4'- and 2:4'-dichlorobenzophenones, which were separated by conversion into the corresponding ketones.

When *o*-chlorobenzoic chloride is treated with chlorobenzene and

aluminium chloride, it is converted into 2:4'-*dichlorobenzophenone*, which crystallises in colourless prisms, melts at 66·5—67°, and is identical with the ketone of lower melting point obtained from carbon tetrachloride. By the action of phosphorus pentachloride on this ketone, 2:4'-*dichlorobenzophenone chloride* is obtained as an oil which boils at 223° under 23 mm. pressure.

4:4'-*Dichlorobenzophenone chloride* crystallises in prisms, melts at 52—53°, boils at 223° under 18 mm. pressure, and is readily soluble in light petroleum.

A study has been made of the best conditions for the condensation of carbon tetrachloride with *p*-dichlorobenzene, as a result of which an improved method is described for the preparation of 2:5:2:5'-tetra-chlorobenzophenone chloride. E. G.

Synthesis of Dihalogen Derivatives of Benzophenone. F. BOBROUX (*Compt. rend.*, 1903, 137, 710—712).—*p*-Chloro- and *p*-bromo-phenyl magnesium bromides react in ethereal solution with carbon dioxide, forming a halogen-benzoic acid and a di-derivative of benzophenone, the latter compound predominating at the boiling point of ether and the former at low temperatures. C. H. D.

Synthesis of a Benzoyl-*m*-xlenol. ADOLFO LINARI (*Gazzetta*, 1903, 33, ii, 60—65. Compare Bartolotti and Linari, *Abstr.*, 1902, i, 792; 1903, i, 177).—*Benzoyl*-1:3:4-*xlenol*, $C_6H_2BzMe_2 \cdot OH$, was prepared by the action of benzoyl chloride, in presence of sodium hydroxide, on 1:3:4-*xlenol*, and was purified by conversion into the *benzoyl* compound, $C_6H_2BzMe_2 \cdot OBz$, by the action of benzoyl chloride and zinc chloride in chloroform solution, and subsequent treatment of this product with alcoholic sodium hydroxide. It crystallises from alcohol in shining, white scales melting at 145—146° and dissolves slightly in alkali hydroxide solutions, to which it imparts a yellow colour. Its *methyl* derivative, $C_6H_2BzMe_2 \cdot OMe$, separates from alcohol in large, colourless prisms melting at 52·5—53·5°, and its *dibromo*-derivative, $C_6Br_2BzMe_2 \cdot OH$, is deposited from aqueous alcohol in mammillary masses of colourless crystals melting at 161—162°.

T. H. P.

Condensation Products of Dibenzyl Ketone and Benzaldehyde. GUIDO GOLDSCHMIEDT and KARL SPITZAUER (*Monatsh.*, 1903, 24, 720—728. Compare *Abstr.*, 1899, i, 140; 1900, i, 35; Stoermer and Wehln, *Abstr.*, 1903, i, 40).— $\alpha\beta\delta\epsilon$ -Tetraphenyl-pentane- γ -one- $\alpha\epsilon$ -diol forms a *diacetate*, $CO(CHPh \cdot CHPh \cdot OAc)_3$, which crystallises in delicate, white needles and melts at 180—181°, and a *dibenzoate*, which crystallises in glistening, white needles and melts at 136°. $\alpha\beta\delta$ -Triphenylbutane- γ -one- α -ol forms an *acetate*,



which crystallises in clusters of needles and melts at 109—111°, and a *benzoate*, which melts at 147—149°.

The action of hydrogen chloride on a mixture of dibenzyl ketone and benzaldehyde leads to the formation of benzylidenedibenzyl

ketone, which melts at 163° and is obtained instead of 1:2-diphenyl-tetrahydro- β -naphthenone by the action of potassium hydroxide on its additive compound with hydrogen chloride. In one experiment, the action of hydrogen chloride lead to the formation of an isomeric ketone, $C_{22}H_{18}O$, which melts at 86° and dissolves in sulphuric acid to an emerald-green solution. G. Y.

Addition of Acids to $\alpha\beta$ -Unsaturated Ketones. DANIEL VORLÄNDER and M. HAYAKAWA (*Ber.*, 1903, **36**, 3528—3546. Compare Vorländer and Mumme, *Abstr.*, 1903, i, 495).—Unsaturated ketones of the type $R\cdot CH:CH\cdot CO\cdot CH:CH\cdot R$ give with acids two mono-additive compounds, which may be represented by the formulæ A , $R\cdot CH(XH):CH\cdot CO\cdot R$ and B , $R\cdot CHX\cdot CH_2\cdot CO\cdot R$ (or $R\cdot CH_2\cdot CHX\cdot CO\cdot R$).

With two molecules of acid, three compounds are obtainable, to which the formulæ: $2A$, $R(HX)\cdot CO\cdot R(HX)$; $2B$, $R\cdot HX\cdot CO\cdot RHX$; AB , $R(HX)\cdot CO\cdot RHX$, are given. The compounds of the type A are coloured and relatively unstable; sometimes they can be isolated, but in many cases their formation is evident only from their colour, since they are readily transformed into colourless compounds of the type B . The acid may be regarded as combined as such in compounds of the A form, as it can be removed quantitatively by simply digesting the additive compound with water for several hours at the ordinary temperature, whilst for the removal of the acid, the additive compound of the B form requires to be heated for 4—5 hours with aqueous alcoholic sodium hydroxide.

On passing dry hydrogen bromide into cooled benzylidenepinacolin, a golden-yellow liquid is obtained, which soon solidifies to a crystalline mass; on recrystallising the product from ether, the *hydrobromide B*, $C_{13}H_{17}OBr$, separates in white needles melting at 44° . It rapidly loses hydrogen bromide when kept, and is reconverted into benzylidenepinacolin; it is thus similar to the hydrochloride already described (*loc. cit.*).

Phorone gives only additive compounds of the B type; the *dihydrobromide B*, $C_{19}H_{14}O\cdot 2HBr$, prepared by passing hydrogen bromide through phorone at 0° , forms white plates melting at 19° ; the *dihydrochloride B* can only be obtained as a liquid which loses acid only very slowly when shaken with water; when distilled four times, however, it is completely reconverted into phorone.

The *monohydrobromide A* of dibenzylideneacetone separates in small, orange-coloured needles on first passing hydrogen bromide into a solution of the ketone in dry benzene or light petroleum; it becomes orange-red at 95° , melts at 100° , and decomposes at 115° ; if an excess of hydrogen bromide is used, the *dihydrobromide 2A* is obtained in red crystals, which are very unstable, and are immediately and completely decomposed by cold water giving dibenzylideneacetone. When the *dihydrobromide A* is exposed to moist air or kept in a desiccator over soda-lime, it regenerates the monohydrobromide A . The *dihydrobromide 2B* is prepared by passing hydrogen bromide through a solution of dibenzylideneacetone in light petroleum for 4 hours, when most of the coloured hydrobromide which first separates redissolves;

on evaporating the solution and crystallising the product from ether or glacial acetic acid, white leaflets are obtained, which become orange at 65—73° and melt and decompose at 124—126°. The same substance is obtained when hydrogen bromide is passed over dry benzylideneacetone for 8 hours; hydrogen chloride, however, under the same conditions, gives rise almost exclusively to the orange dihydrochloride 2A (compare *loc. cit.*).

The *monohydrobromide* A of dianisylideneacetone is obtained as a brown precipitate on passing hydrogen bromide into a solution of the ketone in benzene; it melts and decomposes at 165°, and is easily converted by an excess of the acid into the violet *dihydrobromide* 2A; with a great excess of sulphuric acid (100 mols.), anisylideneacetone combines to form a crystalline, reddish-violet *dihydrosulphate*, $C_{19}H_{18}O_8, 2H_2SO_4$.

Dicinnamylidenecyclopentanone combines with hydrogen bromide to form a black *dihydrobromide* 2A. With bromine (1 mol.) in ice-cold chloroform solution, dicuminyldieneacetone yields a *dibromide*, $C_{23}H_{26}OBr_2$, which separates from ether in white crystals, melts at about 110°, and decomposes at 138°; with 2 mols. of bromine, the *tetrabromide*, $C_{23}H_{26}OBr_4$, is obtained, which forms white needles and melts at 189°.

W. A. D.

Benzoylfluorene. GUSTAVE PERRIER (*Monatsh.*, 1903, 24, 591—592). GUIDO GOLDSCHMIEDT (*ibid.*, 592—594. Compare Fortner, *Abstr.*, 1903, i, 177).—A question of priority. Perrier has previously described (*Thèse inaugurale*, Paris, 1896) the preparation of benzoylfluorene (m. p. 123°), its oxime (m. p. 208°), and the corresponding secondary alcohol (m. p. 113°).

G. Y.

Aromatic Hydroxy-ketones. KARL AUWERS (*Ber.*, 1903, 36, 3890—3892).—The following compounds were prepared by condensing phenetole and *p*-tolyl ethyl ether by means of aluminium chloride with various acid chlorides and hydrolysing the ethers so obtained by Hartmann and Gattermann's method (*Abstr.*, 1893, i, 152).

p-Hydroxy-*i*-valerophenone, $OH \cdot C_6H_4 \cdot CO \cdot C_4H_9$, crystallises from ether in rhombic prisms and melts at 97—98°. *p*-Hydroxypalmitophenone, $OH \cdot C_6H_4 \cdot CO \cdot C_{15}H_{31}$, separates from light petroleum in slender needles melting at 78°. 3'-Nitro-4-hydroxybenzophenone forms yellow prisms, melts at 173°, and gives an *ethyl ether* which crystallises from a mixture of absolute alcohol and light petroleum in slender, white prisms and melts at 79—81°. 1'-Nitro-4-hydroxybenzophenone was not obtained pure; its *ethyl ether* crystallises from alcohol in dark yellow prisms melting at 115°. 6-Hydroxy-3-methylpropio-phenone, $OH \cdot C_6H_3Me \cdot CO \cdot C_3H_7$, melts at -2° and boils at 135—140° under 22 mm. pressure. 6-Hydroxy-3-methyl-*n*-butyrophenone crystallises from dilute alcohol in slender, rhombic prisms, melts at 34°, and gives an *ethyl ether* which boils at 205° under 100 mm. pressure. 6-Hydroxy-3-methylbenzophenone forms yellow leaflets melting at 84°, and its *ethyl ether* forms yellow needles and melts at 68°. 4'-Nitro-6-hydroxy-3-methylbenzophenone crystallises from alcohol in thin, yellow plates and melts at 142—143°.

W. A. D.

Preparation and Hydrolysis of Phenol Ethers by Gattermann's Method. KARL AUWERS (*Ber.*, 1903, 36, 3893—3902).—When *p*-nitrobenzoyl chloride is condensed with phenetole in carbon disulphide solution by means of aluminium chloride, 4'-nitro-4-ethoxybenzophenone, melting at 112°, is the principal product, but 4'-nitro-2-hydroxybenzophenone is also always formed, together with traces of 4'-nitro-4-hydroxybenzophenone; it is probable that the former of these phenols owes its origin to the hydrolysis by aluminium chloride of the corresponding ether, formed simultaneously with 4'-nitro-4-ethoxybenzophenone, although this could not be isolated. An alternative explanation would be the wandering of the radicle $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot$ from the para- into the ortho-position relatively to the hydroxyl, but there is little evidence to favour such an assumption.

4'-Nitro-2-hydroxybenzophenone crystallises in slender, yellow prisms and melts at 111—113°. 4'-Nitro-4-hydroxybenzophenone, prepared by hydrolysing its ethyl ether by means of aluminium chloride in carbon bisulphide solution, crystallises in slender, yellow needles, and after softening at 182° melts at 190—192°; in this hydrolysis, not a trace of the isomeric 4'-nitro-2-hydroxy-compound is formed. 4'-Nitro-4-acetoxybenzophenone crystallises from alcohol in long needles and melts at 131°.

When anisole is condensed with *p*-nitrobenzoyl chloride under the foregoing conditions, the principal product is 4'-nitro-4-methoxybenzophenone, which crystallises from alcohol or glacial acetic acid in white needles, melts at 121°, and on hydrolysis behaves normally, giving 4'-nitro-4-hydroxybenzophenone only.

The constitution of 4'-nitro-4-hydroxybenzophenone was established by reducing it to the corresponding amino-derivative and converting this into 4:4'-dihydroxybenzophenone. From 4'-nitro-4-methoxybenzophenone, in a similar manner, 4'-hydroxy-4-methoxybenzophenone was obtained; it crystallises from hot water or toluene in lustrous needles, melts at 151—152°, and on methylation gives 4:4'-dimethoxybenzophenone (Bösler, *Abstr.*, 1881, 421).

4'-Nitro-2-methoxybenzophenone, prepared by methylating the phenol melting at 111—113°, crystallises from alcohol or light petroleum in lustrous, flat prisms or plates and melts at 117—119°. 4':2-Dihydroxybenzophenone was obtained from the same substance by reduction and subsequent diazotisation, thus proving the structure of the phenol.

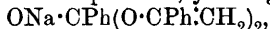
W. A. D.

Transformation of Acetophenone *O*-Benzoate into Dibenzoylmethane. LUDWIG CLAISEN and EMIL HAASE [and, in part, with A. BEHRE] (*Ber.*, 1903, 36, 3674—3682. Compare *Abstr.*, 1897, i, 188).—Lee's *O*-benzoylated acetophenone [α -benzoxy- α -phenylethylene] (*Trans.*, 1903, 83, 145) has been obtained in the form of crystals melting at 41°.

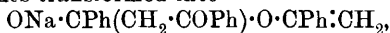
When a mixture of acetophenone, benzoyl chloride, and pyridine is left for 6—7 weeks at the ordinary temperature, a compound, $\text{C}_{20}\text{H}_{17}\text{O}_2\text{N}$, is obtained. It crystallises in small, yellow prisms, melts at 110°, and decomposes above 230°. When hydrolysed, it yields acetophenone, benzoic acid, and pyridine.

Dibenzoylmethane, in the form of its sodium derivative, may be

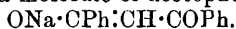
obtained by warming a benzene solution of the *O*-benzoyl derivative with sodium wire and a small amount of sodioacetophenone. To obtain dibenzoylmethane itself, the mass is extracted with water and the aqueous solution decomposed by carbon dioxide. The mechanism of the reaction is probably first the addition of the *O*-benzoylacetophenone molecule to sodioacetophenone, yielding the compound



which then becomes transformed into



and this, by the loss of a molecule of acetophenone, yields



When dibenzoylmethane is benzoylated by the aid of benzoyl chloride and pyridine, it yields an *O*-benzoyl derivative, $\text{OBz}\cdot\text{CPh}\cdot\text{CHBz}$, melting at $108-109^\circ$. When this is heated for several hours at $230-240^\circ$, it yields benzoic acid and a compound, $\text{C}_{15}\text{H}_{10}\text{O}$, melting at $225-230^\circ$ and insoluble in acetone.

A summary of the modes of formation and properties of the various benzoyl derivatives of methane is given. J. J. S.

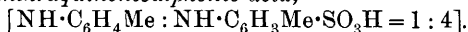
[Dinitrophenyl Ether of Quinoneoxime.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 144765).—When nitrosophenol is heated in alcoholic solution with a molecular proportion of 1-chloro-2 : 4-dinitrobenzene in presence of sodium acetate or carbonate, condensation takes place to *quinoneoxime dinitrophenyl ether*, $\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$, a crystalline compound melting and decomposing at 165° , insoluble in dilute acids or alkalis. Gentle reducing agents, as sodium sulphide, form *p*-aminophenol and 2 : 4-dinitrophenol. Fusion with sulphur and sodium sulphide converts it into a black dye. C. H. D.

o-Methoxyanthraquinonesulphonic Acids. FARBWERKE VORM. MEISTER, LUCIUS, and BRÜNING (D.R.-P. 145188).—*Sodium-1-methoxyanthraquinone-6-sulphonate*, $\text{NaSO}_3\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix}\text{C}_6\text{H}_3\cdot\text{OMe}$, prepared by heating together sodium α -nitroanthraquinonesulphonate, sodium hydroxide, methyl alcohol, and water in a reflux apparatus, is a yellowish-brown, crystalline powder, dissolving in water. When heated with sulphuric acid at 120° , it is hydrolysed, forming 1-hydroxyanthraquinone-6-sulphonic acid. The sodium salt of this acid, when heated with calcium hydroxide under pressure, forms 1 : 6-dihydroxyanthraquinone, crystallising from dilute alcohol in large, yellow needles melting at 260° and dissolving in concentrated sulphuric acid and dilute alkalis to yellowish-red solutions. The constitution follows from the fact that all the other dihydroxyanthraquinones are known, and is confirmed by the oxidation of α -aminoanthraquinonesulphonic acid by potassium permanganate to 1 : 2 : 4-sulphophthalic acid, proving that the sulpho- and methoxy-groups are in different rings.

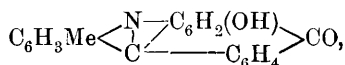
When β -nitroanthraquinonesulphonic acid is treated in this way, *sodium 1-methoxyanthraquinone-7-sulphonate* is obtained as a yellowish-brown powder. When heated with lime under pressure, *m*-benzodihydroxyanthraquinone is formed. β -Aminoanthraquinonesulphonic acid is oxidised to the same sulphophthalic acid as the α -compound.

C. H. D

New Anthracene Dyes. PAUL FRIEDLÄNDER and G. SCHICK (*Zeit. Farb. Text. Chem.*, 1903, 2, 429—430).—Alizarincyanin-green, when reduced with stannous chloride, gives dihydroquinizarin, *p*-toluidine, and *p*-toluidinesulphonic acid; it therefore has the constitution of a *di-p-toluidinoanthraquinonesulphonic acid*,



Alizarinirisol is similarly shown to be *4-hydroxyanthraquinone-1-p-toluidinosulphonic acid* $[\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{SO}_3\text{H} : \text{OH} = 1 : 4]$. When heated with 60 per cent. sulphuric acid, it is converted into an *acridine* derivative,



which crystallises from glacial acetic acid in brownish-black leaflets and is strongly fluorescent.

W. A. D.

Nitro-derivatives of Phenanthraquinone. JULIUS SCHMIDT (*Ber.*, 1903, 36, 3726—3730).—A summary of the principal results contained in the four following papers.

C. H. D.

The Phenanthrene Series. VII. 2-Nitrophenanthraquinone and its Derivatives. JULIUS SCHMIDT and PATRIC C. AUSTIN (*Ber.*, 1903, 36, 3730—3734).—2-Nitrophenanthraquinone is best prepared by boiling phenanthraquinone with concentrated nitric acid for 2 minutes and immediately pouring into cold water. On crystallising from glacial acetic acid, the 2-nitro-compound separates first, and the mother liquor deposits, on evaporation, the 4-nitro-compound (see following abstract).

2-Nitrophenanthraquinoneoxime forms greenish-yellow needles which melt and decompose at 213°, softening previously. 2-Nitro-9:10-dihydroxyphenanthrene, prepared by reduction of the quinone, forms small, brownish-yellow crystals, decomposing slowly on heating and then melting at about 220°; it dissolves in dilute aqueous sodium hydroxide to a brownish-violet solution. Even traces give a reddish-violet solution in concentrated sulphuric acid. The *diacetyl* derivative forms bright yellow needles softening at 250° and melting at 258°. The quinone is oxidised by heating with a mixture of concentrated sulphuric acid and potassium dichromate to *p-nitrodiphenic acid*, crystallising from water in glistening, white leaflets melting at 214—216° and dissolving readily in alcohol or ether, less readily in hot water or benzene. Tin and hydrochloric acid reduce it to *p-aminodiphenic acid*, crystallising from water, and melting and decomposing at 277°.

3-Nitrophenanthraquinone (Schmidt and Kämpf, *Abstr.*, 1902, i, 797) is oxidised to *m-nitrodiphenic acid*, crystallising from water in white, silvery leaflets melting at 268°.

C. H. D.

The Phenanthrene Series. VIII. 4-Nitrophenanthraquinone and its Derivatives. JULIUS SCHMIDT and ADOLF KÄMPF (*Ber.*, 1903, 36, 3734—3738).—4-Nitrophenanthraquinone has not been previously prepared, the substance obtained by Kehrman and Kikine (*Abstr.*, 1900, i, 61) being a mixture containing 4:5-dinitrophenanthraquinone. Prepared as described in the preceding abstract, it

forms bright yellow groups of needles melting at 179—180° after repeated recrystallisation from alcohol. When precipitated from sulphuric acid solution by water, it dissolves in dilute alkali hydroxides to a yellow solution, from which it is precipitated unaltered by acids. Its constitution is proved by its ready conversion by boiling with fuming nitric acid into 4:5-dinitrophenanthraquinone (see following abstracts). The *oxime* crystallises from alcohol in greenish-yellow needles melting at 169—170°. The cold alcoholic solution is coloured dark reddish-brown by ferric chloride. On boiling an alcoholic solution of the quinone with *o*-phenylenediamine hydrochloride, *o*-nitrodiphenylenequinoxaline, $C_6H_4 \begin{matrix} N:C_6H_4 \\ | \\ N:C_6H_3NO_2 \end{matrix}$, is formed, crystallising from benzene in hair-like needles melting at 217—218°. Hydrogen sulphide or phenylhydrazine readily reduces the quinone to the quinol, which is unstable, but may be converted into the acetyl derivative by boiling with acetic anhydride. 4-Nitro-9:10-diacetoxyphenanthrene crystallises from 60 per cent. acetic acid in white needles melting and decomposing at 222—223°.

4-Nitrophenanthraquinone may be oxidised by chromic acid in the same way as the 2-nitro-compound, forming *o*-nitrodiphenic acid, crystallising from 30 per cent. acetic acid in large, white leaflets melting and decomposing at 248—250°, dissolving readily in alcohol, ether, acetone, or glacial acetic acid, sparingly in benzene, chloroform, or light petroleum. The salts of the alkaline earth metals are soluble, those of lead and silver insoluble. Unlike the dinitrodiphenic acids, the acid has no bitter taste. Tin and hydrochloric acid reduce it to *o*-aminodiphenic acid, which forms white needles, very sparingly soluble in water and remaining unmelted at 300°. C. H. D.

The Phenanthrene Series. IX. 2:7-Dinitrophenanthraquinone and its Derivatives. JULIUS SCHMIDT and ADOLF KÄMPF (*Ber.*, 1903, 36, 3738—3744).—2:7-Dinitrophenanthraquinone (*Abstr.*, 1902, i, 797) forms an *oxime*, which crystallises in slender, yellow needles melting at 246—248°, at the same time becoming green and evolving gas. 4:4'-Dinitrodiphenylenequinoxaline crystallises from benzene in almost white needles melting at 356°. Alcoholic ammonia converts the quinone into 2:7-dinitrophenanthraquinoneimide, crystallising from alcohol in brownish-yellow needles melting and decomposing at 358—360°. 2:7-Dihydroxyphenanthraquinone, prepared by boiling the diazonium compound of 2:7-diaminophenanthraquinone (compare Anschütz and Meyer, *Abstr.*, 1885, 1067), is a dark brownish-red powder melting above 400° and dissolving readily in alcohol, acetone, or glacial acetic acid to reddish-violet solutions, less readily in ether or ethyl acetate, very sparingly in benzene. Alkali hydroxides dissolve it to a green solution, from which carbon dioxide again precipitates it. The solution in concentrated sulphuric acid is greenish-brown, giving a black precipitate with potassium dichromate, again dissolving on addition of more dichromate. The *diacetyl* derivative crystallises from glacial acetic acid in glistening red tablets, melting and decomposing at 235—236°.

An attempt to synthesise the dinitroquinone from 4:4'-dinitrodiphenic acid was made. 4:4'-Dinitrodiphenic chloride separates from benzene in white crystals melting at 138°. Heating with copper powder at 265° produced no condensation; at 290°, explosive decomposition occurred. The presence of the two nitro-groups appears to cause mutual repulsion of the carboxyl groups, thus hindering the anhydride formation. C. H. D.

The Phenanthrene Series. X. 4:5-Dinitrophenanthraquinone and its Derivatives. JULIUS SCHMIDT and ADOLF KÄMPF (*Ber.*, 1903, 36, 3745—3752).—4:5-Dinitrophenanthraquinone, obtained in the preparation of the 2:7-isomeride, melts after repeated treatment with hot fuming nitric acid at 228°. Chromic acid oxidises it to 2:2'-dinitrodiphenic acid (compare Schultz, *Abstr.*, 1880, 814), which is well suited to its identification. Anhydride formation does not take place. When mixed with sand and distilled at 300° under 30 mm. pressure, 2:2'-dinitrodiphenyl is produced, together with a small quantity of a sparingly soluble compound melting at 240°, probably dinitrofluorenone.

2:2'-Diaminodiphenic acid, prepared by reduction of the dinitroacid with tin and fuming hydrochloric acid, is very insoluble in water. When mixed with barium hydroxide and distilled, carbazole is produced, thus confirming the constitution assigned to the dinitrocompound.

4:5-Dinitrophenanthraquinoneoxime crystallises from alcohol in yellow clusters, melting and decomposing at 190—191°. 2:2'-Dinitrodiphenylenequinoxaline forms pale red needles melting at 262—264°. When the quinone is heated with fuming sulphuric acid on the water-bath, no sulphonic acid is formed, but 2:2'-dinitrodiphenic acid is obtained, the reaction thus resembling the oxidation of naphthalene to phthalic acid.

4:5-Dinitro-9:10-diacetoxypheanthrene, which forms white needles, melts at 258°, the dibenzoyl derivative melts at 210°.

Tin and fuming hydrochloric acid reduce the dinitroquinone to 4:5-diamino-9:10-dihydroxypheanthrene, which is unstable, its hydrochloride forms large, white needles which darken superficially on drying. On adding an excess of potassium carbonate to the solution and passing a current of air, 4:5-diaminophenanthraquinone is precipitated in black flocks, and may be obtained in indefinite crystals, melting at about 235°, by solution in alcohol. Attempts to obtain intramolecular condensation, or combination, with α -diketones were unsuccessful. 4:5-Dihydroxypheanthraquinone forms dark red crystals charring at 400° without previous fusion. It is more readily soluble in organic solvents than the 2:7-derivative. The solution in concentrated sulphuric acid is brownish-red, giving no characteristic reaction with potassium dichromate. 4:5-Dimethoxypheanthraquinone separates from dry ether in dark red crystals melting at 190—191° after softening, dissolving readily in benzene or glacial acetic acid, less readily in ethyl or methyl alcohol. The dibenzoyl derivative crystallises from alcohol in slender, yellow needles melting at about 170°. C. H. D.

Interaction of Mercuric Acetate with Terpenes and Compounds containing the C_3H_5 Group. II. LUIGI BALBIANO and VINCENZO PAOLINI (*Ber.*, 1903, **36**, 3575—3584. Compare Abstr., 1902, i, 808).—The compound, $C_{10}H_{16}O_2$, prepared by the action of mercuric acetate on pinene is converted into carvacrol by warming with dilute sulphuric acid, thus proving the position of the hydroxyl-group, whilst its oxidation to terpenylic acid proves the position of the carbonyl group; it is therefore a 6-hydroxy- Δ^6 -menthen-2-one, $CH_3 \cdot C \begin{smallmatrix} \swarrow C(OH) \cdot CH_2 \\ \searrow CO-CH_2 \end{smallmatrix} > CH \cdot CHMe_2$, and a hydroxy-derivative of Harries' menthenone (Abstr., 1901, i, 551), but it could not be reduced.

[With GION VESPIGNANI].—The same compound is produced from *d*-pinene.

Camphene yields a compound, $C_{10}H_{16}O(Hg \cdot OAc)_2$, which crystallises in glistening, white, odourless flakes and melts at 188—189°; hydrogen sulphide reconverts it into camphene, and this is also formed on attempting to reduce it with sodium amalgam or with zinc and potassium hydroxide. The mercurichloride, $C_{10}H_{16}O(HgCl)_2$, is a white, odourless powder, insoluble in neutral solvents, and softens at 150°, but does not melt at 250°.

Pinene thus behaves as a propenyl, and camphene as an allyl compound, in accordance with the formulæ $CH \begin{smallmatrix} \swarrow CMe \cdot CH- \\ \searrow CH_2-CH- \end{smallmatrix} > CH_2$ and

$CH_2 \cdot CH \cdot CMe_2$
 $\left| \begin{smallmatrix} CH_2 \\ CH_2 \cdot CH \cdot C:CH_2 \end{smallmatrix} \right|$, since the propenyl compounds are oxidised by

mercuric acetate, whilst allyl compounds yield additive products. Thus, on covering a saturated solution of mercuric acetate with benzene containing two or three drops of a propenyl compound such as anethole, methylisoeugenol, or isosafrole, mercurous acetate separates in 15 to 45 minutes, whilst with an allyl compound such as methylchavicol, methyleugenol, or safrole, the two layers remain clear for two or three days; apiole gives an immediate precipitate of the insoluble additive compound, but this in no way resembles the characteristic flakes of mercurous acetate. The additive products have the general formula $R \cdot C_3H_5(OH) \cdot Hg \cdot OAc$, and are mixtures of two isomerides which can sometimes be separated by conversion into the corresponding chlorides, but cannot usually be reduced to the hydroxypropyl compounds, $R \cdot C_3H_6 \cdot OH$, as these are unstable and readily lose a molecule of water.

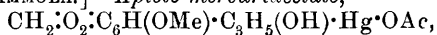
[With ENRICO LUZZI].—Safrole yields the crystalline additive compound, $CH_2 \cdot O_2 \cdot C_6H_3 \cdot C_3H_5(OH) \cdot Hg \cdot OAc$, which is converted by sodium chloride into the mercurichloride, $CH_2 \cdot O_2 \cdot C_6H_3 \cdot C_3H_5(OH) \cdot HgCl$, a white, crystalline powder, insoluble in water and sparingly soluble in boiling alcohol, which blackens and decomposes at 170°, and is reduced by zinc and sodium hydroxide to safrole. The syrupy, isomeric mercuriacetate yields a mercurichloride which crystallises from alcohol in rosettes of hard, glistening, prismatic needles, melts at 138°, and

solidifies to a glassy mass, and is reduced to safrole by zinc and sodium hydroxide. *iso*Safrole reduces the mercuric to mercurous acetate and is oxidised to the glycol, $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{C}_3\text{H}_5(\text{OH})_2$, which crystallises in stout crystals and melts at $101\text{--}102^\circ$ (Wagner and Bouschmakin, Abstr., 1892, 310); prolonged oxidation in warm weather yields a yellow, aromatic liquid, $\text{C}_{10}\text{H}_{10}\text{O}_3$, which boils at 142° under 23 mm. pressure; its *oxime* crystallises in needles and melts at 89° , and its *semicarbazone* crystallises in colourless flakes and melts at 158° .

[With U. TONAZZI.]—Methylchavicol, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2$, an allyl isomeride of anethole, obtained from *Dracuncuti* oil, boils at $214\text{--}216^\circ$, and has n_D 1.5244 at 15° . The mixture of *mercuri-acetates* forms a thick syrup, of which a part becomes crystalline after some months and is separated by conversion into the corresponding chlorides and bromides. The chief *mercurichloride* is insoluble in water but dissolves in alcohol, and crystallises in white, glistening needles and melts at $81\text{--}82^\circ$; the *isomeride*, a resinous mass insoluble in alcohol, gradually hardens, and when heated, softens at 55° without showing a definite melting point; both are reduced to methylchavicol. The *mercuribromide* crystallises in white needles, melts at 70° , and is also accompanied by a resinous isomeride.

[With F. BERNARDINI.]—Methyleugenole forms a syrupy *mercuri-acetate*, $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{C}_3\text{H}_5(\text{OH})\cdot\text{Hg}\cdot\text{OAc}$, which gradually solidifies to a mass of radiating needles. The crystalline *mercurichloride* forms small, hard, colourless prisms, is insoluble in water, but soluble in alcohol and melts at $112\text{--}113^\circ$; the resinous isomeride was not examined, but both are reduced to methyleugenole. Methyl *isoeugenole* yields the *glycol*, $(\text{OMe})_2\text{C}_6\text{H}_3\cdot\text{C}_3\text{H}_5(\text{OH})_2$, which forms prismatic plates and melts at $120\text{--}121^\circ$; the *bisphenylcarbamide* crystallises from boiling alcohol in colourless needles and melts at $166\text{--}168^\circ$. An isomeric *glycol* is also produced which crystallises from ether in glistening prisms and melts at $88\text{--}89^\circ$ (compare Kolokoloff, *J. Russ. Phys. Chem. Soc.*, 1897, 29, 23).

[With G. MAMMOLA.]—*Apiole mercuriacetate*,



crystallises from alcohol in minute needles and melts at $157\text{--}158^\circ$. It is reduced by zinc and sodium hydroxide to the *compound*, $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}(\text{OMe})_2\cdot\text{C}_3\text{H}_5\cdot\text{OH}$, which crystallises in glistening needles and melts at $29.5\text{--}30.5^\circ$; the *benzoyl* derivative is a viscous liquid which boils at 165° under 4 mm. pressure, and solidifies when cooled with ice to a mass of needle-shaped crystals, but again melts at ordinary temperatures. *iso**Apioleglycol*, $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}(\text{OMe})_2\cdot\text{C}_3\text{H}_5(\text{OH})_2$, prepared by the action of mercuric acetate on *iso*apiole, crystallises from ether in colourless needles and melts at 120° ; it combines with phenylcarbimide and with benzoyl chloride, but the products were not purified. It also combines with mercuric acetate to form the *compound*, $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6(\text{OMe})_2[\text{C}_3\text{H}_5(\text{OH})_2]\cdot\text{Hg}\cdot\text{OAc}, \text{OAcHg}$, which crystallises in colourless flakes, softens at 160° , and melts and decomposes at 174° .

T. M. L.

Pulegone Nitrosite. PAUL GENVRESSE (*Compt. rend.*, 1903, 137, 494—495).—*Pulegone nitrosite*, $\text{C}_{10}\text{H}_{16}\text{O}_4\text{N}_2$, prepared by the action

of nitrogen peroxide, or "nitrous fumes," on a well-cooled solution of pulegone in light petroleum, crystallises in colourless, silky needles, melts at 68—69°, is soluble in cold alcohol, more so in chloroform, slightly volatile in steam, and has $[\alpha]_D + 23.13^\circ$ in chloroform at 23°. The nitrosite gives with phenol and sulphuric acid a brilliant emerald-green coloration, does not decolorise bromine, and furnishes an oily *oxime*, but does not react with piperidine or benzylamine.

T. A. H.

Terpenes and Ethereal Oils. Pulenone [1:4:4-Trimethyl-5-hexanone]. OTTO WALLACH [with WILHELM KEMPE and, in part, FRITZ COLLMANN, J. MEYER, and H. SONNEBORN] (*Annalen*, 1903, 329, 82—108).—Pulegenic acid, which has a five-membered ring (Abstr., 1903, i, 569), is readily converted by oxidation to a hydroxy-lactone, and by subsequent treatment with sulphuric acid into a cyclic ketone, pulenone, which has now been shown to be a trimethylhexanone, $\text{CMe}_2 \begin{smallmatrix} \text{CH}_2-\text{CO} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CHMe}$. Under the influence of the sulphuric acid, the five-membered ring in the lactone of pulegenic acid is broken, carbon dioxide eliminated, and a six-membered ring formed.

Pulenone is best prepared from pulegenic acid (Abstr., 1898, i, 484) as follows: the acid is converted into the hydroxy-lactone (m. p. 129—130°) by oxidising a dilute alkaline solution with 4 per cent. permanganate; the hydroxy-lactone is then distilled under reduced pressure with sulphuric acid, when carbon dioxide is evolved at 80° and the pulenone passes over; the ketone boils at 183°, has a sp. gr. 0.8925 and n_D 1.44506 at 21°.

Pulenol, $\text{C}_9\text{H}_{17}\cdot\text{OH}$, is prepared by reducing the ketone by sodium in moist ether, and boils at 187—189°, and has sp. gr. 0.8955 and n_D 1.4569 at 20°. With phenylcarbimide, it forms a *urethane*, $\text{C}_9\text{H}_{17}\cdot\text{O}\cdot\text{CO}\cdot\text{NHPh}$, which melts at 84—85° or 92°.

Pulenene, C_9H_{16} , is prepared by heating pulenol with potassium hydrogen sulphate at 150°, and distilling the product in steam; it is an isomeride of pulegene, and is an oil boiling at 60—65° under 12 mm. pressure; the *additive* product with nitrosyl chloride is prepared by adding a solution of the hydrocarbon and amyl nitrite in acetic acid to a cold solution of hydrogen chloride in acetic acid and forms colourless crystals melting at 98—99°. When pulenol is heated with zinc chloride at 160—170°, a *hydrocarbon* boiling at 145—150° under ordinary pressure is obtained; it yields no solid nitrosochloride.

When pulenone is oxidised with permanganate, acetic acid is formed together with a non-volatile ketonic acid, which melts at 115°, and *as*-dimethylsuccinic acid (m. p. 140°). If the oxidation is carried out with chromic acid in sulphuric acid solution, three acids are formed: a *ketonic acid*, $\text{C}_8\text{H}_{14}\text{O}_3$, melting at 49—50°, *as*-dimethylsuccinic acid, and *aa* δ -trimethyladipic acid, $\text{CO}_2\text{H}\cdot\text{CHMe}\cdot[\text{CH}_2]_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$, which melts at 115°; when its calcium salt is distilled with soda-lime, it is converted into *trimethylpentanone*, $\text{CMe}_2 \begin{smallmatrix} \text{CO}-\text{CHMe} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix}$, an oil boiling

at 152—153°; the *semicarbazone* of this cyclic ketone melts at 150—151° and the *oxime* at 60—62°. When the pentanone is oxidised by chromic acid, it is converted into the same ketonic acid (m. p. 49—50°) as is obtained by the direct oxidation of pulenone; its *semicarbazone* melts at 163°. Since it is oxidised by potassium hypobromite to $\alpha\alpha$ -dimethylglutaric acid (m. p. 82°), it can only be γ -acetyl- $\alpha\alpha$ -dimethylbutyric acid, $\text{CH}_2\text{Ac}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$. Further, both pulenone and the dimethylglutaric acid yield on oxidation dimethylsuccinic acid.

By the action of phosphorous oxychloride on pulenoneoxime (which melts at 94—95° and boils at 117° under 12 mm. pressure), a feebly basic *isooxime* is obtained; it forms crystals melting at 96—97° and boils at 145—150° under 27 mm. pressure, and cannot be converted into an amide by acids.

When boiled with acetic anhydride, pulenoneoxime loses water and yields a *nonenonitrile*, $\text{C}_8\text{H}_{15}\cdot\text{CN}$, which is an oil boiling at 89—90° under 10 mm., or at 216—217° under the ordinary pressure; it is converted into *nonenoic acid*, $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, by heating with sodium methoxide in alcoholic solution under pressure at 180°; the acid is a liquid boiling at 143—147° under 23 mm. pressure, and has a sp. gr. 0.9435 and n_D 1.4561 at 20°; its constitution is demonstrated by the fact that it is oxidised by permanganate to acetone and β -methylglutaric acid. The *isooxime* can also be converted into this nonenoic acid by heating under pressure with sulphuric acid; the *isooxime* consequently has the constitution $\text{CHMe}\begin{matrix} \text{CH}_2\text{--CO--NH} \\ \diagdown \\ \text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}_2 \end{matrix}$, and when hydrolysed is first converted into the amide of a hydroxy-acid, which then loses $2\text{H}_2\text{O}$, becoming the nitrile of nonenoic acid.

The view is expressed that in the conversion of pulenoneoxime into nonenonitrile the phases, *isooxime* and amide of hydroxy-acid, are formed intermediately. This supposition accounts for the differences observed in the behaviour of cyclic ketone oximes; thus the oxime of menthone yields most readily an amide, since in this case the *isooxime*, first formed, gives a hydroxy-acid, which from the position of the hydroxyl group does not readily lose water. In the case of camphoroxime on the other hand, the nitrile is produced even under the influence of dilute acids.

K. J. P. O.

Essential Oil of Petit Grain. PAUL JEANCARD and C. SATIE (*Bull. Soc. Chim.*, 1903, [iii], 29, 1088—1093. Compare Abstr., 1900, i, 511, and 1902, i, 45).—The authors have examined specimens of petit grain oil, distilled at intervals of a week during the month of June, in each of the years 1901, 1902, and 1903. The specific gravities, rotatory powers, solubilities in 70 per cent. alcohol, viscosities, acid, and saponification numbers, and percentage of alcohols of these oils are tabulated in the original. These tables indicate that both the rotatory power and viscosity of the oils are lower in colder seasons. By comparison of specimens of oil distilled in January (when only 1.4 per cent. of oil is

obtained) and in June, respectively, it was ascertained that the specific gravity, lævo-rotation, viscosity, and saponification numbers decrease during the first six months of the year and during the same period the oil becomes more soluble in 70 per cent. alcohol and the content of free alcohols increases. During the second half of the year, these changes are reversed, the alcohols being replaced by esters, whence it appears that a rising temperature increases both the yield of oil and the amount of free alcohols contained in it, whilst a falling temperature leads to the replacement of the alcohols by their esters. In orange flowers (yielding neroli oil), the formation of esters appears to be independent of the formation of alcohols, whilst in the branches (yielding petit grain oil) the total alcohol (uncombined and in the form of esters) is the same both in January and June. T. A. H.

The Alban of Gutta-percha. ALEXANDER TSCHIRCH (*Arch. Pharm.*, 1903, 241, 481—495).—A specimen of gutta-percha at least 20 years old, which had become brittle, was extracted thoroughly with boiling 96 per cent. alcohol. The alban, which separated from the alcoholic extracts on cooling, was separated by fractional crystallisation into *spherite-alban*, $C_{30}H_{44}O_2$, which melts at 152° , crystallises in spherites, and dissolves in hot alcohol, although not in cold, and *crystal-alban*, $C_{60}H_{80}O_3$, which melts at $227.5\text{--}228^\circ$, crystallises in plates, and dissolves with difficulty even in boiling alcohol. The residual gutta-percha was dissolved in chloroform, the solution filtered, $3/4$ of the chloroform distilled off, and the residual solution poured into alcohol; the liquid was filtered from the sticky gutta which separated, and the filtrate allowed to remain, when flocculent aggregates separated, consisting of tiny needles of albanan (see later). In 100 parts of the substance were contained approximately: crystal-alban, 15; spherite-alban, 30; albanan, 0.1.

From a fresh sample of commercial gutta-percha, spherite-alban was obtained, but no crystal-alban; in place of the latter, an isomeride of the former, *isospherite-alban*, $C_{30}H_{44}O_2$, was obtained; it melts at 142° , crystallises in needles or in spherites built up of needles, and dissolves in alcohol at 60° . A larger quantity of *albanan*, $C_{30}H_{44}O$, was obtained than from the old specimen; it melted at 61° , and was entirely insoluble in alcohol. In 100 parts of the sample were contained approximately: spherite-alban, 30; *isospherite-alban*, 8; albanan, 1.

Several colour reactions of these substances are described.

Structural formulæ are suggested for them, the substances being represented as oxypolyterpenes. C. F. B.

Resin-Balsam of Pinus Laricio Poiret (Austrian Turpentine). ALEXANDER TSCHIRCH and GEORG SCHMIDT (*Arch. Pharm.*, 1903, 241, 570—588).—From a solution of the resin in ether, 1 per cent. aqueous ammonium carbonate extracts slowly (500 shakings were necessary for complete extraction) amorphous monobasic *laricopinic acid*, $C_{21}H_{30}O_3$, melting at $75\text{--}80^\circ$, and with acid number 177 and saponification

number about 230. One per cent. aqueous sodium carbonate then extracts crystalline monobasic *laricopinonic acid*, $C_{20}H_{28}O_4$, melting at 97° , and with acid number 183 and saponification number about 230; the anhydrous *silver*, *lead*, and *barium* salts were analysed; the acid could not be made to yield an acetyl derivative. From the remaining ethereal solution of the resin, 1 per cent. aqueous potassium hydroxide extracted nothing further. After complete extraction with potassium hydroxide, the ether was evaporated and the residue distilled with steam; an *essential oil* passed over slowly (5 months' distilling was necessary for complete separation), which for the most part boiled at $155\text{--}160^\circ$ and had a sp. gr. 0.872; there remained behind a *resen* which could not be purified satisfactorily.

The resin itself had acid number 115 and saponification number about 120; it contained no *p*-coumaric acid, nor could a methoxyl group be detected in it. Water extracts a *bitter substance*. In the product of the dry distillation of the resin, formic, acetic, and succinic acids were detected; in the distillation of the mixed resin-acids, retene was obtained. Both the resin-acids were optically inactive. In 100 parts of the resin were contained: laricopinic acid, 25; laricopinonic acid, 34; essential oil, 35; resen, 2; water, bitter substance, and impurities, 3—4 parts.

A list is given below of the acids isolated up to the present by Tschirch and his collaborators from the resins of coniferous plants; those of one group were separated by extracting the ethereal solution of the resin with 1 per cent. aqueous ammonium carbonate, those of the other by subsequent extraction with 1 per cent. sodium carbonate. It is noteworthy that nearly all of them contain 2 atoms of oxygen in the molecule, and so must be either monocarboxylic or dihydroxy-compounds; in their power of forming salts, they behave as monobasic acids. Those not marked with an asterisk in the list exhibit a "saponification number" distinct from the acid number; it has been pointed out, however, that this is due, not to the hydrolysis of an ester, but to the slow fixation of more potash. Abietic acid may be taken as the type of the acids of this class; for the most part, they are derived from the genus *Abies*, and crystallise in plates. The acids marked with an asterisk have no "saponification number," or, rather, they have one practically identical with the acid number; of this class, pimaric acid may be taken as the type. These acids are derived for the most part from the genera *Picea* and *Dammara*, and are either amorphous or crystallise in rather shapeless aggregates. As a rule, any one resin contains only acids belonging to one of these two classes.

| Acid. | Melting point. | Percentage of | | Formula. | Acid number (direct). | Saponification number (hot). |
|---|----------------|---------------|------|--|-----------------------|------------------------------|
| | | C. | H. | | | |
| <i>Isolated by means of ammonium carbonate.</i> | | | | | | |
| *Picipimarinic..... | 130—135° | 73·5 | 10·2 | C ₁₂ H ₂₀ O ₂ | 287 | 288 |
| *Mancopalic..... | 175 | 68·4 | 8·4 | C ₈ H ₁₂ O ₂ | 398 | 398 |
| *Mancopalenic..... | 100—105 | 67·8 | 9·7 | C ₈ H ₁₄ O ₂ | 392 | 392 |
| Palabienic | 110 | 75·3 | 9·3 | C ₁₃ H ₂₀ O ₂ | 188 | 235 |
| *Kauric..... | 192 | 72·0 | 9·2 | C ₁₀ H ₁₆ O ₂ | 330 | 335 |
| *Canadic | 135—136 | 77·3 | 11·9 | C ₁₉ H ₃₄ O ₂ | 192 | 192 |
| *Piceapimarinic .. | 130—132 | 75·1 | 9·4 | C ₁₃ H ₂₀ O ₂ | 262 | 262 |
| *Pimarinic | 118—119 | 75·8 | 10·0 | C ₁₄ H ₂₂ O ₂ | 252 | 255 |
| Abienic | 114—115 | 74·9 | 9·2 | C ₁₃ H ₂₀ O ₂ | 176 | 258 |
| Laricopinic | 75—80 | 76·4 | 9·1 | C ₂₁ H ₃₀ O ₃ | 177 | 243 |
| α -Abietic..... | 155 | 78·9 | 9·6 | C ₁₉ H ₂₈ O ₂ | 176 | 246 |
| β -Abietic..... | 158 | 79·0 | 9·5 | C ₁₉ H ₂₈ O ₂ | 174 | 189 |
| Beljiabienic | 113—115 | 75·0 | 9·3 | C ₁₃ H ₂₀ O ₂ | 182 | 255 |

Isolated by means of sodium carbonate.

| | | | | | | |
|-------------------------------|-----------|------|------|-------------------|-----|-----|
| * α -Mancopalic .. | 85—90° | 70·4 | 10·6 | $C_{10}H_{18}O_2$ | 326 | 330 |
| * β -Mancopalic .. | 83—88 | 70·4 | 10·5 | $C_{10}H_{18}O_2$ | 323 | 330 |
| α -Palabietinolic .. | 90—95 | 77·4 | 9·6 | $C_{16}H_{24}O_2$ | 194 | 312 |
| β -Palabietinolic... | 90—95 | 77·2 | 9·5 | $C_{16}H_{24}O_2$ | 190 | 299 |
| * α -Kaurolic | 81—83 | 73·4 | 10·1 | $C_{12}H_{20}O_2$ | 279 | 282 |
| * β -Kaurolic | 85—87 | 73·3 | 10·1 | $C_{12}H_{20}O_2$ | 278 | 283 |
| *Silveolic | 138 | 76·2 | 9·3 | $C_{14}H_{20}O_2$ | 224 | 228 |
| Canadolic | 143—145 | 79·2 | 9·7 | $C_{19}H_{28}O_2$ | 192 | 328 |
| Laricinolic | 147—148 | 79·4 | 9·7 | $C_{20}H_{30}O_2$ | 190 | 396 |
| Abietolic | 145—153 | 79·9 | 9·6 | $C_{20}H_{28}O_2$ | 189 | 350 |
| Laricopinonic..... | 97 | 72·3 | 8·4 | $C_{20}H_{28}O_4$ | 181 | 257 |
| * γ -Abietic | 153—154 | 79·1 | 9·8 | $C_{19}H_{28}O_2$ | 182 | 183 |
| *Pimaric | 144—146 | 79·4 | 9·9 | $C_{20}H_{30}O_2$ | 186 | 186 |
| *Piceapimaric .. | 144—145 | 79·5 | 9·9 | $C_{20}H_{30}O_2$ | 192 | 191 |
| Palabietic | 153—154 | 79·1 | 9·9 | $C_{19}H_{28}O_2$ | 182 | 321 |
| α -Abietinolic | 95—96 | 77·3 | 9·5 | $C_{16}H_{24}O_2$ | 218 | 286 |
| β -Abietinolic | 93—94 | 77·2 | 9·4 | $C_{16}H_{24}O_2$ | 217 | 266 |
| α -Larinolic | 80—81 | 78·9 | 9·7 | $C_{18}H_{26}O_2$ | 199 | 316 |
| β -Larinolic | 85—86 | 78·7 | 9·7 | $C_{18}H_{26}O_2$ | 196 | 302 |
| * α -Canadinolic..... | 95 | 78·6 | 10·6 | $C_{19}H_{30}O_2$ | 200 | 261 |
| * β -Canadinolic..... | 95 | 78·6 | 10·6 | $C_{19}H_{30}O_2$ | 198 | 199 |
| * α -Piceapimarolic .. | 95 | 79·8 | 11·6 | $C_{25}H_{44}O_2$ | 166 | 166 |
| * β -Piceapimarolic .. | 94 | 79·6 | 11·7 | $C_{25}H_{44}O_2$ | 165 | 165 |
| * α -Pimarolic..... | 90—91 | 78·7 | 9·6 | $C_{18}H_{26}O_2$ | 196 | 195 |
| * β -Pimarolic | 89—96 | 78·8 | 9·3 | $C_{18}H_{26}O_2$ | 196 | 199 |
| * α -Silvinolic..... | below 100 | 75·8 | 11·0 | $C_{15}H_{26}O_2$ | 230 | 233 |
| * β -Silvinolic | below 100 | 75·0 | 10·9 | $C_{14}H_{24}O_2$ | 244 | 251 |
| * α -Picipimarolic .. | 95—96 | 78·2 | 10·4 | $C_{18}H_{28}O_2$ | 200 | 200 |
| * β -Picipimarolic .. | 93—94 | 78·6 | 10·3 | $C_{18}H_{28}O_2$ | 206 | 207 |
| Beljiabietic..... | 153—154 | 79·3 | 9·8 | $C_{19}H_{28}O_2$ | 182 | 333 |
| α -Beljiabietinolic. | 95—96 | 77·7 | 9·8 | $C_{16}H_{24}O_2$ | 210 | 274 |
| β -Beljiabietinolic. | 95—96 | 77·7 | 9·8 | $C_{16}H_{24}O_2$ | 210 | 257 |

* Has no "saponification number."

† Or $C_{20}H_{30}O_2$.

C. F. B.

American Colophony. ALEXANDER TSCHIRCH and B. STUDER (*Arch. Pharm.*, 1903, 241, 495—522).—A solution of the resin in ether was shaken repeatedly with 1 per cent. aqueous ammonium carbonate; after 300—400 repetitions, a constant amount of acid, equal to 0.025 per cent. of the resin, was dissolved each time, and as about the same amount continued to be dissolved up to the 600th repetition, the process was then discontinued. Attempts to obtain the crystalline acid by using a mixture of methyl and ethyl alcohols or light petroleum as a solvent were unsuccessful. At last, it was found possible, by treating an alcoholic solution of the acid with alcoholic lead acetate, to effect a separation into a lead salt insoluble in alcohol and an acid which remained in solution without forming a lead salt at all. The corresponding acids can then be crystallised separately from alcohol; they appear to be isomeric and to have the molecular formula $C_{19}H_{28}O_2$. The first, *α -abietic acid*, softens at 143° and is completely melted at 155° , and is a monobasic acid, with acid number 177 and saponification number 247. The second, *β -abietic acid*, softens at 145° and is completely melted at 158° , and is a monobasic acid, with acid number 174 and saponification number 190.

From the ethereal solution of the resin, 1 per cent. aqueous sodium carbonate now extracted another acid, *γ -abietic acid*, isomeric with the first two; the extraction was complete after 20 operations. This acid melts at 153 — 154° , but probably at 161° when pure; it has $[\alpha]_D - 37.75^\circ$ and is monobasic, with acid number 183 and saponification number 186; when heated with hydriodic acid, it does not evolve methyl iodide, and it is not changed when boiled with acetic anhydride; it was distilled to a large extent unchanged in an iron apparatus under diminished pressure. The behaviour of each of these three acids towards the usual cholesterol reagents is described; a *silver* salt of each was prepared and analysed.

From the residual ethereal solution, neither 1 nor 10 per cent. aqueous sodium hydroxide extracted any further acid. The ether was evaporated, and the residue distilled with steam; the distillation had to be continued for $1\frac{1}{2}$ months to drive over all the *essential oil*, although but little of this was present. The *resen* remaining could only be obtained as a brown mass that softened in the hand, and therefore was not analysed.

From 100 parts of the resin were obtained, approximately (the loss in manipulation being about 10 per cent.): abietic acids, α 30, β 22, γ 32; essential oil, 0.4—0.7; resen, 5—6; impurities, 0.1. A small quantity of an amorphous *bitter substance* could be extracted with water.

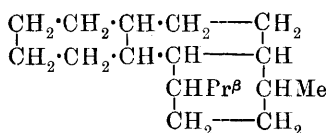
An examination was made of the abietic acid obtained by previous investigators, namely, that obtained by Maly, by washing the resin with 70 per cent. alcohol until white, and then crystallising it from strong alcohol; by Flückiger, by leading dry hydrogen chloride into an alcoholic solution of the resin; and by Tschirch, by extracting an ethereal solution of the resin with aqueous sodium hydroxide. The acid obtained by the first method was actually separated into the three isomeric acids described above.

Fahrion (*Abstr.*, 1902, i, 165) has shown that the part of colo-

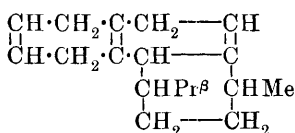
phony less soluble in light petroleum has a higher ester number, and that this part increases in amount when the resin is exposed in the state of powder to light and air; he attributes this to autoxidation. It may be merely molecular transformation, for the α -abietic acid, which has a high ester number, is less soluble in light petroleum than the two isomeric acids, which have no ester number, or a very low one.

A table is given of the acid and saponification numbers of 13 samples of American colophony; in the case of some of the samples, the percentage insoluble in light petroleum is also indicated. C. F. B.

Constitution of Abietic Acids. ALEXANDER TSCHIRCH and B. STUDER (*Arch. Pharm.*, 1903, 241, 523—545).—The reactions of the resin-acids of *Coniferæ* are discussed, and the various formulæ proposed for them are considered. The conclusion is drawn that Tschirch's view of them (*Pharm. Post*, 1900, No. 43; *J. de Pharm. et de Chim.*, Nov. 1900), as derived from fichtelite or from a hydrogenised retene, octohydroretene, has most in its favour; "it is in harmony with all the observed facts and is contradicted by none of them."



Fichtelite.



Octohydroretene.

On account of the undoubted relation of the resin-acids to the cholesterol, phytosterols are more likely than tannins to be the parent substances of these acids. But no impassable gulf is fixed between the two classes of compounds; some of the resinotannols, substances resembling tannins, in some reactions yield derivatives of benzene; in others, derivatives of terpenes, and, consequently, they may be regarded as containing a combination of a benzene with a terpene ring.

C. F. B.

Rhein from Aloe-emodin. OTTO A. OESTERLE (*Arch. Pharm.*, 1903, 241, 604—607).—Aloe-emodin was oxidised with chromic acid in boiling acetic acid solution, the liquid poured into water, and the precipitate dried and extracted with chloroform in a Soxhlet apparatus. The residue was found to be identical with the rhein of rhubarb (Hesse, *Abstr.*, 1900, i, 41; Tschirch and Heuberger, *Abstr.*, 1903, i, 108). Much of the emodin escaped oxidation. C. F. B.

Solanin. SIMON ZEISEL and J. WITTMANN (*Ber.*, 1903, 36, 3554—3558).—A criticism of Hilger and Merckens (*Abstr.*, 1903, i, 846). The formation of crotonaldehyde on decomposing solanin by dilute sulphuric acid is doubted; the only aldehyde formed is methyl-furfuraldehyde in small quantity. The sugar obtained from solanin does not consist exclusively of dextrose, but contains a large proportion

of rhamnose as well as another carbohydrate, which is not easily isolated. Crystalline dextrose cannot be obtained from the mixture of sugars. W. A. D.

Ceroptene. WALTER C. BLASDALE (*J. Amer. Chem. Soc.*, 1903, 25, 1141—1152).—The fronds from *Gymnogramme triangularis*, the "golden-back" fern of the Pacific coast, were extracted with benzene or light petroleum and, from the extract, crystals of ceroptene separated. The mother liquor, from which the ceroptene had been removed, contained cerotic acid. *Ceroptene*, $C_{18}H_{18}O_4$, forms tabular or prismatic triclinic crystals [$a:b:c=8.5353:1:1.0138$; $\alpha=112^\circ13'$, $\beta=92^\circ12'$, $\gamma=94^\circ33'$] of a sulphur-yellow colour, melts at 135° , and has a sp. gr. 1.1976 at $15^\circ/15^\circ$. It is readily dissolved by dilute solutions of alkali hydroxides; its *potassium*, *barium*, *silver*, and *lead* salts are described. The *iodo*-derivative, prepared by the action of hydriodic acid on a solution of ceroptene in glacial acetic acid at 60° , separates in needles and melts at 182° . A. McK.

Brazilin and Hæmatoxylin. JOSEF HERZIG and JACQUES POLLAK (*Ber.*, 1903, 36, 3713—3715. Compare Abstr., 1902, i, 482; 1903, i, 270, 508, 713).—Acetyltetramethylhæmatoxylin on oxidation yields tetramethylhæmatoxylone, which reacts with hydroxylamine hydrochloride, forming a compound having the composition of an *oxime*, $C_{20}H_{20}O_6 \cdot N \cdot OH$. The *acetyl* derivative melts and decomposes at 179 — 183° . The methods adopted by the authors for the preparation of isomeric dehydro-derivatives from trimethylbrazilone (*loc. cit.*, 508) have also been applied in this case. Direct acetylation yields *α*-acetyltetramethyldehydrohæmatoxylin, melting at 194° , the action of sulphuric acid produces the *β*-compound, melting at 194 — 195° , a mixture of the two melting at 168 — 182° , a *γ*-compound could not be prepared. *α*-Pentamethyldehydrohæmatoxylin, prepared by the action of diazomethane on the *α*-tetramethyl derivative, melts at 168 — 170° , the *β*-compound at 175 — 176° , a mixture of the two at 145 — 155° . The two *β*-compounds are identical with those obtained by Kostanecki and Rost (this vol., i, 646), and described as derivatives of 5-(or 10-)hydroxy-1:2:7:8-tetramethoxybrazan, the melting points differ slightly from those given by these authors. C. H. D.

Theory of Dyeing. GEORG VON GEORGIEVICS (*Ber.*, 1903, 36, 3787—3790).—A criticism of Binz and Schröter's paper on the same subject (Abstr., 1903, i, 109; see also 1902, i, 635). E. F. A.

Sulphur Dyes from the Phenols and their Derivatives. CHEMISCHE FABRIK GRÜNAU; LANDSHOFF & MEYER, AKTIEN-GESELLSCHAFT (D.R.-P. 144104).—Compounds such as phenols, nitro- and amino-phenols, and diphenylamine derivatives, which yield dyes on fusion with alkali sulphide and sulphur, also form dyes when mixed with sodium hydroxide and sodium thiosulphate and heated at 200 — 280° . C. H. D.

Derivatives and Oxidation Products of Nitropyromucic Acid. R. MARQUIS (*Compt. rend.*, 1903, 137, 520—521).—*Methyl nitropyromucate*, prepared by the method already described for the ethyl ester (*Abstr.*, 1903, i, 49), crystallises in nacreous lamellæ, melts at 78.5°, and is more soluble in alcohol than the ethyl ester.

Nitropyromucyl chloride, obtained by the action of phosphorus pentachloride on nitropyromucic acid dissolved in chloroform, crystallises in greasy lamellæ, melts at 38°, is soluble in chloroform and ether, and is slowly decomposed by cold water. The *amide* forms white, silky crystals and melts at 161°. The *anilide* crystallises in citron-yellow needles and melts at 180°. The *p-toluidide* forms yellow prisms and melts at 162°.

When oxidised by sodium peroxide, ethyl nitropyromucate furnishes fumaric acid, indicating that the nitro-group occupies either the 3- or 4-position (compare *Abstr.*, 1903, i, 49, and Hill and White, *Abstr.*, 1902, i, 388).

T. A. H.

Esters of isoPyromucic Acid. G. CHAVANNE (*Compt. rend.*, 1903, 137, 992—993).—*isoPyromucic acid* is not readily esterifiable (*Abstr.*, 1901, i, 649), but the sodium salt, prepared by the action of sodium methoxide on the acid in methyl alcoholic solution, reacts on warming gently with ethyl or methyl sulphate. The ester formed is purified by crystallisation from dry ether. *Methyl isopyromucate*, $C_5H_3O_3Me$, forms long, colourless needles melting at 60° and boiling at 130—135° under 20 mm. pressure. *Ethyl isopyromucate* melts at 52°, and may also be distilled under reduced pressure. *Benzyl isopyromucate* forms highly refractive prisms melting at 71°, and may be prepared in small yield by the direct action of benzyl chloride on sodium isopyromucate. The methyl and ethyl esters are very soluble in water or alcohol, less so in ether, the benzyl ester is insoluble in water, but dissolves readily in organic solvents. They become yellow on exposure to light, and are very stable towards acids, resembling phenyl ethers rather than esters.

C. H. D.

Quinonoid Derivatives of Benzopyranol from 3:5-Dimethoxybenzoylacetophenone. II. CARL BÜLOW and GUSTAV RIESS (*Ber.*, 1903, 36, 3607—3610. Compare *Abstr.*, 1903, i, 101, 647, 715).—3:5-Dimethoxybenzoylacetophenone condenses with pyrogallol in glacial acetic acid in presence of hydrogen chloride, forming 4:7-anhydro-7:8-dihydroxy-2-phenyl-4-di-m-methoxyphenyl-1:4-benzopyranol hydrochloride, $C_{23}H_{18}O_5 \cdot HCl \cdot H_2O$, which crystallises from acidified alcohol in reddish-brown needles. The *base*, obtained by the treatment of an alcoholic solution of the hydrochloride with sodium acetate, crystallises in bluish-black needles melting at 225—230°, and dissolving in benzene or chloroform to a blue solution, insoluble in water or dilute sodium hydroxide. The *picrate* forms groups of small needles melting and decomposing at 215—218°.

Phloroglucinol yields a similar derivative, 5:7-dihydroxy-2-phenyl-4-di-m-methoxyphenyl-1:4-benzopyranol, crystallising in brownish-red needles melting at 215—220°. The *hydrochloride* forms brick-red needles decomposing at 205°. Picric acid precipitates the *picrate* of

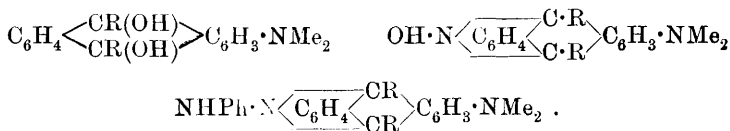
the anhydrobenzopyranol from alcoholic solution in vermilion crystals melting and decomposing at 205°.

C. H. D.

Condensation Products of Tetramethyldiaminophenyl-oxanthranol with Benzene, Toluene, and Dimethylaniline. ALBIN HALLER and ALFRED GUYOT (*Compt. rend.*, 1903, 137, 606—611. Compare Abstr., 1901, i, 350; 1903, i, 200, 348).—When a mixture of equal parts of benzene and tetramethyldiaminophenyl-oxanthranol (Abstr., 1899, i, 350) is treated with five times its weight of sulphuric acid, there is formed an *additive product*, $C_{30}H_{30}O_2N_2$. This separates from benzene solution on adding light petroleum in colourless crystals, melts at 140°, is soluble in benzene and chloroform, and slightly so in alcohol and ether. Its *salts* are crystalline, and dissolve in water to form intensely orange-coloured solutions; the *zinc chloride* derivative forms red crystals. With hydroxylamine, a *condensation product*, $C_{30}H_{29}ON_3$, is obtained, which crystallises in slender needles and melts at 210°. The corresponding *substance*, $C_{36}H_{34}N_4$, produced by condensation with phenylhydrazine, forms colourless crystals and melts at 200°.

Similarly, when toluene is condensed with tetramethyldiaminophenyl-oxanthranol, a *product*, $C_{31}H_{32}O_2N_2$, is obtained, which forms colourless crystals, melts at 163—164°, and has solubilities similar to those of its lower homologue. The *salts* are crystalline, and give intense orange-red aqueous solutions. The derivative, obtained by condensation with hydroxylamine, forms slender, colourless needles and melts at 245°, and that with phenylhydrazine, pale yellow crystals melting at 220°.

To these additive products and their hydroxylamine and phenylhydrazine derivatives respectively, the authors assign formulæ of the following type:



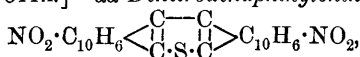
in which R may be either phenyl or tolyl. Similar formulæ have already been assigned by the authors to phthalyl-green, produced by condensing dimethylaniline with tetramethyldiaminophenyl-oxanthranol and its corresponding derivatives (Abstr., 1903, i, 200). T. A. H.

The Union of Dinaphthaxanthonium Salts with Phenols. ROBERT FOSSE (*Compt. rend.*, 1903, 137, 858—860).—Dinaphthaxanthonium salts, $CH \begin{array}{c} \diagup C_{10}H_6 \\ \diagdown C_{10}H_6 \end{array} OX$, interact with sodium compounds of phenols to give derivatives of *p*-hydroxyphenyldinaphthaxanthen, $OH \cdot C_6H_4 \cdot CH \begin{array}{c} \diagup C_{10}H_6 \\ \diagdown C_{10}H_6 \end{array} O$; the same compounds can also be obtained by the condensation of one molecule of a hydroxybenzaldehyde with two molecules of β -naphthol. Thus *p*-hydroxyphenylnaphthaxanthen is

formed (a) from dinaphthaxanthonium chloride and sodium phenoxide, (b) from *p*-hydroxybenzaldehyde and β -naphthol, the product melts at 207° and crystallises with one molecule of alcohol. Analogous methods led to the formation of 4-hydroxy-3-methoxyphenylnaphthaxanthen melting at 210° , and of 2-hydroxynaphthyl-naphthaxanthen, which melts at 273° . S. S.

Decacyclene [Trinaphthylbenzene] and Dinaphthylthiophen. II. KARL DZIEWOŃSKI (*Ber.*, 1903, 36, 3768—3774. Compare Abstr., 1903, i, 431).—[With PAUL BACHMANN.]— α -Bromodinaphthylthiophen, $C_{10}H_6 \begin{smallmatrix} \text{C} & \text{C} \\ | & | \\ \text{C} & \text{S} & \text{C} \end{smallmatrix} C_{10}H_5Br$, prepared by the action of bromine on dinaphthylthiophen, crystallises from chloroform in small, bulky, red needles and melts at 202° . The α -dibromo-derivative, $C_{24}H_{10}SBr_2$, crystallises from nitrobenzene in glistening, red needles and melts at 362 — 363° . Both compounds yield α -bromonaphthalic anhydride, $C_{10}H_5Br \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{C} & \text{O} \end{smallmatrix}$, when oxidised with chromic acid.

[With ELIGIO DOTTA.]— α -Dinitrodinaphthylthiophen,



crystallises from nitrobenzene in small, grey-violet needles, and, when heated, sublimes and partially decomposes; it yields α -nitronaphthalic anhydride, $NO_2 \cdot C_{10}H_5 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{C} & \text{O} \end{smallmatrix}$, when oxidised.

Trinitrodecacyclene, $C_{36}H_{15}(NO_2)_3$, forms red, glistening needles, is almost insoluble in all solvents but quinoline, and, when heated, explodes (puffs) without melting or subliming.

Tribromodecacyclene, $C_{36}H_{15}Br_3$, crystallises from nitrobenzene in minute, yellow needles, softens at 380° , and melts at 397 — 400° .

Nonochlorodecacyclene, $C_{36}H_9Cl_9$, is a yellow powder, much more soluble than the preceding compounds, and melts at 215 — 218° .

T. M. L.

Alkaloids of Angostura Bark. HEINRICH BECKURTS and GUSTAV FRERICHS (*Chem. Centr.*, 1903, ii, 1010—1011; from *Apoth. Zeit.*, 18, 697—699. Compare Abstr., 1892, 642).—The crystalline alkaloids of angostura bark, cusparine, galipine, galipidine, and cusparidine are stronger bases than the amorphous alkaloids of the bark, and may be separated from the ethereal extract by means of their tartrates or acetates. Galipidine is a tertiary base and forms a methyl derivative. The yellow colour of its salts is due to the presence of a small quantity of galipine, which disappears when the alkaloid is submitted to the action of nascent hydrogen; the base then melts at 113° . Cusparine, $C_{20}H_{19}O_3N$, is also a tertiary base containing a methoxyl group, but no hydroxyl groups; it forms a methyl derivative. When fused with potassium hydroxide, it does not decompose directly into a base and an aromatic acid (compare Körner and Boehringer, Abstr., 1884, 341), but by the action of the heat alone is converted into the base pyrocusparine, melting at 350° , which is then attacked by the

alkali and yields protocathechuic acid. When cusparine is heated with carbimide for a short time only, pyrocusparine is formed together with a *base* which melts at 142° . Galipidine also yields protocathechuic acid, and, like cusparine, is not readily hydrolysed. *Nitrocusparine*, prepared by the action of dilute nitric acid on cusparine, crystallises in yellow needles.

After separating the crystalline alkaloids from the ethereal extract by shaking with dilute hydrochloric acid or from a solution in light petroleum by means of picric acid, another alkaloid, cuspareine, may be isolated from the liquid bases which are left. One hundred kilograms of bark yield 7 grams of this alkaloid. *Cuspareine*, $C_{34}H_{36}O_2N_5(?)$, is soluble in light petroleum, crystallises in needles, melts at 54° , and boils with slight decomposition at about 300° . It does not form salts, but gives a deep red coloration with oxidising agents, and combines with methyl iodide. The liquid bases from which cuspareine has been extracted distil without decomposition at higher temperatures, but attempts to prepare crystalline salts failed.

When narceine is melted with carbimide (compare Abstr., 1903, i, 717), the ammonia liberated by the decomposition of the latter compound converts the former into narceineimide and an indifferent compound which melts at 192° . Berberine, under similar conditions, yields an alkaloid which forms yellow salts and serves as an excellent indicator for alkalis, ammonia, and carbonates, and also for the titration of alkaloids in presence of a layer of chloroform. Morphine, strychnine, and papaverine are not affected by melting with carbimide.

E. W. W.

Preparation of Caffeine-ethylenediamine. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 142896).—*Caffeine-ethylene-diamine*, prepared by heating chloro- or bromo-caffeine with ethylenediamine in alcoholic solution, separates from alcohol in crystals melting at 184° and dissolves readily in water, hot chloroform, or alcohol. The *acetyl* derivative melts at 282° and the *lactyl* derivative at 240° . A small quantity of the sparingly soluble dicaffeine-ethylenediamine is formed at the same time.

C. H. D.

Chemistry of Chelidonine. JULIUS O. SCHLOTTERBECK and HAROLD C. WATKINS (*Pharm. Arch.*, 1903, 6, 141—144. Compare Abstr., 1902, ii, 100).—Chelidonine, $C_{20}H_{19}O_5N \cdot H_2O$, melts at 136° and has $[\alpha]_D +115^{\circ}24'$. Its *acetyl* derivative, $C_{20}H_{18}O_4N \cdot OAc$, crystallises in white plates and melts at 161° ; the corresponding *benzoyl* derivative melts at 217° . When the alkaloid is heated with zinc dust in an atmosphere of hydrogen, ammonia is produced together with small quantities of a substance which forms small, nodular crystals and has a phenanthrene-like odour. Attempts to oxidise the alkaloid resulted in breaking down the molecule completely with formation of carbon dioxide, ammonia, and probably methylamine, no intermediate product being obtained. Phenylhydrazine does not react with it.

E. G.

A New Isomeric Change of Cinchonine. ZDENKO H. SKRAUP and W. EGERER (*Monatsh.*, 1903, 24, 669—680. Compare Abstr., 1903, i, 649, 715).—When heated with concentrated sulphuric acid at 100° for 45 minutes, cinchonine oxalate yields β -iso- ψ -cinchonine, recognised by comparison of its hydriodide (m. p. 150°) and its hydrochloride with the salts of β -iso- ψ -cinchonine obtained by Pasteur's reaction from β -isocinchonine. When the heating with sulphuric acid is continued for 5 hours, the hydriodide obtained from the product sinters at 150° and melts at 213—214°.

Cinchonine forms an additive compound with hydrogen iodide in the same manner as does cinchonine. The close relationships between cinchonine and β -isocinchonine and between β -isocinchonine and β -iso- ψ -cinchonine have been previously shown. As β -iso- ψ -cinchonine has now been formed from cinchonine through cinchonine, it follows that the "second half" of the cinchonine molecule must closely resemble that of the other cinchonine alkaloids. G. Y.

The Synthesis of Nicotine. AMÉ PICTET (*Compt. rend.*, 1903, 137, 860—862).—The author describes the synthesis of an inactive nicotine (Abstr., 1895, i, 627; 1898, i, 688; 1900, i, 685), which he finds to be identical with that produced by heating an aqueous solution of the sulphate of the natural product. By fractionally crystallising the tartrate of the synthetical base, it is possible to isolate a salt, $C_{10}H_{14}N_2 \cdot 2C_4H_6O_6 \cdot 2H_2O$, which melts at 88° and has $[\alpha]_D + 25.1^\circ$. The base obtained from this tartrate by treatment with sodium hydroxide boils at 246.1° under 735 mm. pressure, has a sp. gr. 1.008 at 22°/4°, and $[\alpha]_D - 161.19^\circ$ at 25.5°. Nicotine derived from natural sources boils at 246.1—246.2° under 730 mm. pressure, has a sp. gr. 1.009 at 20°/4°, and $[\alpha]_D - 161.55^\circ$ at 20°. The synthetical and natural products are therefore identical. S. S.

Methylbetaine of Papaveric Acid. GUIDO GOLDSCHMIEDT and OTTO HÖNIGSCHMID (*Monatsh.*, 1903, 24, 681—705. Compare Schranzhofer, Abstr., 1894, i, 59; Goldschmiedt and Kirpal, Abstr., 1897, i, 131).—Schranzhofer's yellow substance, melting at 192—194°, is now found to be the methylbetaine of papaveric acid as stated by that author. Goldschmiedt and Kirpal were misled by an error in the methoxyl determination (see Abstr., 1903, ii, 578).

The methylbetaine of papaveric acid is formed by the action of methyl iodide on papaveric acid in methyl alcoholic solution at 100°, on papaveric- β -methyl ester alone or in methyl alcoholic solution at 100°, on papaveric- γ -methyl ester in methyl alcoholic solution at 100°, and on papaveric acid in aqueous sodium carbonate solution.

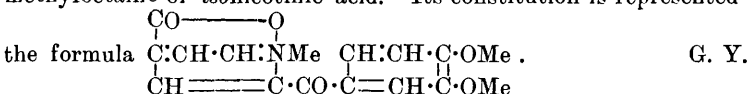
Methyl iodide has no action at 100° on papaveric acid or its γ -methyl ester in absence of a solvent, on dimethyl papavate, or on papaveric anhydride. The methylbetaine is formed by the action of dimethyl sulphate on papaveric acid in aqueous potassium hydroxide solution.

When papaveric- β -methyl ester is heated at its melting point, it yields the γ -methyl ester, which at its melting point decomposes with evolution of carbon dioxide. In neither case is the methylbetaine formed (compare Willstätter, Abstr., 1902, i, 266; Kirpal, Abstr., 1902, i, 564).

The methylbetaine of papaveric acid is not decomposed by boiling fuming hydrochloric acid; when boiled with aqueous barium hydroxide, it yields veratric and apophyllenic acids, and is therefore to be considered to be α -veratrylapophyllenic acid (compare Abstr., Kirpal, 1901, i, 564). A similar hydrolysis takes place with papaveraldine methiodide, which yields veratric acid when boiled with aqueous potassium hydroxide.

The *platinichloride* of the methylbetaine of papaveric acid has the constitution $(C_{17}H_{15}O_7N)_4 \cdot 2HCl \cdot H_2PtCl_6 \cdot 8H_2O$, and the residue, after heating at 125° , $(C_{17}H_{15}O_7N)_4 \cdot H_2PtCl_6$. The *aurichloride*, $C_{17}H_{15}O_7N \cdot HAuCl_4 \cdot H_2O$, crystallises in long, glistening, yellowish-red leaflets.

The methylbetaine of *pyropapaveric acid*, $C_{16}H_{17}O_5N \cdot 3H_2O$, is formed by successive action of methyl iodide and silver oxide on pyropapaveric acid and by heating the methylbetaine of papaveric acid with phenol. It crystallises in white needles, melts at 182° , and is soluble in water or alcohol. The *platinichloride*, $(C_{16}H_{15}O_5N)_2 \cdot H_2PtCl_6 \cdot 2H_2O$, crystallises in glistening, yellow needles and loses $2H_2O$ at 110° . When boiled with aqueous barium hydroxide or potassium hydroxide, the methylbetaine of pyropapaveric acid yields veratric acid and the methylbetaine of isonicotinic acid. Its constitution is represented by



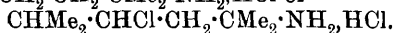
Pyrrolidine-3-carboxylic Acid. HERMANN PAULY and ALEX. HÜLTENSCHMIDT (*Ber.*, 1903, 36, 3351—3370, 3687. Compare Wallach, Abstr., 1902, i, 79).—2 : 2 : 5 : 5-Tetramethylpyrrolidine-3-carboxylic acid, prepared by the action of hydrochloric acid on tetramethylpyrrolidinecarboxylamide (obtained by the action of ammonia on the dibromide of triacetoneamine), crystallises with H_2O in prismatic needles, is easily soluble in water, and melts and decomposes at 220° . The *hydrochloride* forms anhydrous needles easily soluble in water and decomposes at 234° ; the *platinichloride*, $(C_9H_{17}O_2N)_2 \cdot H_2PtCl_6$, decomposes at 216° ; the *methyl ester* is a colourless liquid, boils at 206° (corr.), and has a sp. gr. 0.958 at 24° ; the *ethyl ester* boils at 217° (corr.).

1 : 2 : 2 : 5 : 5-Pentamethylpyrrolidine-3-carboxylic acid, crystallises with $2\frac{1}{2}H_2O$ in plates melting at 129° , and is very easily soluble in water, less so in alcohol; the *hydrochloride* crystallises in prisms and melts and decomposes at 256° ; the *platinichloride* forms orange crystals melting and decomposing at 197 — 198° ; the *methyl ester* boils at 218° (corr.), and its hydriodide melts at 192° ; the ethyl ester boils at 227° (corr.) and has a sp. gr. 0.955 at 15° . The two acids, in contradistinction to the pyrrolidine-2-carboxylic acids (Fischer, Abstr., 1902, i, 699), are almost tasteless; physiologically, the pentamethyl acid is the more powerful poison.

Pentamethylpyrrolidinecarboxylamide forms a *methiodide*, crystallising in flat, prismatic needles and decomposing at 255° ; when heated with potassium hydroxide, this is converted into γ -dimethylamino- α -isopropylideneisohexoamide, $NMe_2 \cdot CMe_2 \cdot CH_2 \cdot C(CMe_2) \cdot CO \cdot NH_2$, which

melts at 98°, boils at 170° under 13 mm. pressure, and crystallises from ether; it yields a sparingly soluble *dibromide* and a *methiodide*, forming prismatic crystals melting at 184°. The latter, when digested with silver oxide and subsequently heated, loses trimethylamine, forming *diisopropylidenepropionamide*, $\text{CMe}_2 \cdot \text{CH} \cdot \text{C}(\text{CO} \cdot \text{NH}_2)_2 \cdot \text{CMe}_2$, which boils at 142—145° under 14 mm. pressure, solidifies to a wax-like substance melting at 59°, and unites with at least two molecules of bromine; the amide is very resistant towards hydrolytic agents.

On heating tetramethylpyrrolidine-3-carboxylic acid at 220°, it is decomposed, a portion distilling over at this temperature, whilst a solid residue remains in the flask. The distillate is ϵ -amino- β -dimethyl- Δ^{β} -hexene, $\text{NH}_2 \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CMe}_2$, which boils at 150°, and forms a *platinichloride*, crystallising in orange-red prisms melting at 172°. When oxidised with permanganate, it yields acetone and β -aminoisovaleric acid. In ethereal solution, it unites with hydrogen chloride to form a sparingly soluble *dihydrochloride*, which may have one of the formulæ $\text{CMe}_2 \cdot \text{Cl} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{NH}_2 \cdot \text{HCl}$ or



With bromine, it forms a *dibromide*, and this yields a *hydrobromide*. The solid residue is 2-dimethyl-4-isopropylidene-5-pyrrolidone,

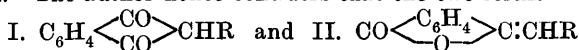
$\text{NH} \begin{array}{c} \text{CMe}_2 \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CO} - \text{C} : \text{CMe}_2 \end{array}$, which crystallises from ether in quadrilateral plates melting at 121°, and forms a *dibromide* melting at 148°.

When heated, pentamethylpyrrolidine-3-carboxylic acid decomposes into ϵ -methylamino- β -dimethyl- Δ^{β} -hexene, boiling at 167—168° and forming an orange-yellow *platinichloride* melting at 160°, and 1 : 2 : 2-trimethyl-4-isopropylidene-5-pyrrolidone, which boils at 127—128° under 15 mm. pressure.

E. F. A.

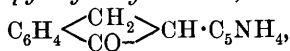
Tetramethylpyrroline-3-carboxylic Acid. HERMANN PAULY and ALEX. HÜLTENSCHMIDT (*Ber.*, 1903, 36, 3371—3372).—When tetramethylpyrroline-3-carboxylic acid is heated at 290—310°, disruption of the ring does not take place, but carbon dioxide is eliminated with the formation of tetramethylpyrroline, $\begin{array}{c} \text{CH} \cdot \text{CMe}_2 \\ | \quad \diagup \\ \text{CH} \cdot \text{CMe}_2 \end{array} > \text{NH}$. E. F. A.

Phthalones. ROBERT GAEBELÉ (*Ber.*, 1903, 36, 3913—3923).—Both pyrophthalone and isopyrophthalone (von Hüber, *Abstr.*, 1903, i, 576) are dissolved by dilute alkali hydroxides, and, on precipitating the salt of the hydroxy-acid obtained in each case with acid, the same substance, namely, the unsymmetrical phthalone, $\text{CO} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{O} \end{array} > \text{C} : \text{CH} \cdot \text{C}_5\text{NH}_4$, is obtained. The author hence considers that the two forms



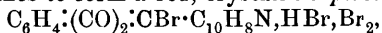
are pseudomeric, and that under the influence of alkali the symmetrical form I undergoes transformation into the form II, which then undergoes fission, forming a hydroxy-acid. This view is supported by the fact that both of the pyrophthalones, on reduction by zinc dust in alkaline solution, give the same *dihydrostilbazole-o-carboxylic acid*,

$C_5NH_4 \cdot CH_2 \cdot CH_2 \cdot C_6H_4 \cdot CO_2H$, the *hydrochloride* of which crystallises from dilute hydrochloric acid and melts at 158° ; on attempting to liberate the acid from the hydrochloride by means of sodium carbonate, an *anhydride*, probably *pyridyl- α -hydrindone*,

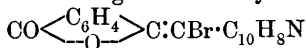


is obtained, which crystallises from alcohol in orange-red needles and melts at $207.5-208^\circ$.

8-Methylquinophthalone, $C_6H_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{CH} \cdot C_{10}H_8N$, prepared by heating 8-methylquinaldine with phthalic anhydride and zinc chloride for 3—4 hours at $180-190^\circ$, crystallises from glacial acetic acid or chloroform in yellow needles, melts at $276.5-277^\circ$, and can be obtained only in one form. With an excess of bromine in chloroform solution, it combines to form a red, crystalline *perbromide*,



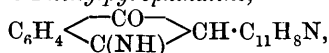
which is decomposed by alcohol giving the *monobromo-derivative*, $C_6H_4 : (CO)_2 : CBr \cdot C_{10}H_8N$. This substance melts at about 170° , but subsequently solidifies to a yellow mass, which melts at $213-215^\circ$; it is suggested that isomeric change to the unsymmetrical form



here occurs.

N-Methyl-8-methylquinophthaline, $C_6H_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ C(NMe) \end{array} \text{CH} \cdot C_{10}H_8N$, prepared by heating 8-methylquinophthalone with alcoholic methylamine for 6—7 hours at 200° , crystallises from chloroform on adding methyl alcohol in red needles and melts at 205° . *N-Ethyl-8-methylquinophthaline* forms orange-red needles melting at 198° , and *N-n-butyl-8-methylquinophthaline*, red needles melting at 178° ; *N-benzyl-8-methylquinophthaline* melts at 208° .

6-Phenylpyrophthalone, $C_{20}H_{13}O_2N$, prepared by condensing 2-methyl-6-phenylpyridine with phthalic anhydride, crystallises from acetic acid or chloroform in golden needles, melts at 263° , and yields, with bromine, an unstable *perbromide*, $C_{20}H_{13}O_2NBr_4$, which, by alcohol, is converted into a yellowish-white *monobromo-derivative* melting at 131° . On reduction with zinc dust and acetic acid, the phthalone is converted into the compound $C_6H_4 \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ CH(OH) \end{array} \text{CH} \cdot C_{11}H_8N$, which crystallises from alcohol in red needles and melts at 135° ; the *hydrochloride* melts at $176-178^\circ$, the *mercurichloride* at 98° , and the *benzoyl derivative*, $C_6H_4 \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ CH(OBz) \end{array} \text{CH} \cdot C_{11}H_8N$, forms small, white leaflets and melts at 155° . *6-Phenylpyrophthaline*,



prepared by heating 6-phenylpyrophthalone with alcoholic ammonia for 7—8 hours at 200° , crystallises from alcohol in red leaflets and melts above 307° .

N-Ethyl-6-phenylpyrophthaline melts at 194° , and gives a *platinichloride* which melts and decomposes at 225° .

N-n-butyl-6-phenylpyrophthaline melts at 168° , and its *platinichloride* at 194° , and *N-benzyl-6-phenylpyrophthaline* melts at 211° . *N-Mesityl-6-phenylpyrophthaline*, prepared from the phthalone and mesidine, forms thick crystals melting at 230° .
W. A. D.

A New Class of Coloured Dithiourethanes. JULIUS VON BRAUN (*Ber.*, 1903, 36, 3520—3527. Compare *Abstr.*, 1902, i, 271).—*Piperidyl-S-benzoyldithiourethane*, $C_5H_{10}N \cdot CS \cdot SBz$, obtained by shaking an aqueous solution of piperidine or piperidyldithiocarbamate with benzoyl chloride (compare *Abstr.*, 1903, i, 13), separates from alcohol in lustrous, yellow crystals and melts at $85-90^{\circ}$; when kept in a sealed vessel for several days or boiled with alcohol for 2—3 minutes, it is converted by loss of carbon disulphide into benzoyl piperidine, which boils at $320-321^{\circ}$, and not at 360° as stated by Schotten (*Abstr.*, 1888, 1105). *Piperidyl-p-anisoyldithiourethane*, $C_5H_{10}N \cdot CS \cdot S \cdot CO \cdot C_6H_4 \cdot OMe$, prepared similarly by using anisic chloride in place of benzoyl chloride, crystallises from alcohol and has a deep yellow colour; it melts at $62-65^{\circ}$ and is more stable at the ordinary temperature than the benzoyl derivative, although when boiled with alcohol it readily gives *anisoylpiperidine*,
 $C_5H_{10}N \cdot CO \cdot C_6H_4 \cdot OMe$,
as a yellow oil boiling at $220-222^{\circ}$ under 14 mm. pressure.

N-Dimethyl-S-benzoyldithiourethane, $NMe_2 \cdot CS \cdot SBz$, melts at 59° and is very unstable, being readily transformed into dimethylbenzamide. *Dimethyl-p-anisoyldithiourethane* is a yellow substance melting at $78-80^{\circ}$.

Attempts to prepare a urethane from diethylamine diethyldithiocarbamate and phenylacetyl chloride gave a deep yellow solution which rapidly became colourless owing to the formation of *phenylacetodiethylamide*, $CH_2Ph \cdot CO \cdot NEt_2$, which boils at $167-168^{\circ}$ under 15 mm. pressure; the urethane formed from propionyl chloride and dipropylamine dipropyldithiocarbamate is equally unstable and is at once resolved into *dipropylpropionamide*, $C_2H_5 \cdot CO \cdot NPr_2$, which boils at $107-108^{\circ}$ under 16 mm. or at 227° under the ordinary pressure.

Ethyl chlorocarbonate gives with piperidine piperidyldithiocarbamate the urethane, $C_5H_{10}N \cdot CO_2Et$, and with dipropylamine dipropyldithiocarbamate, dipropylurethane, $NPr_2 \cdot CO_2Et$ (*Abstr.*, 1902, i, 610). Ethylamine ethyldithiocarbamate and benzoyl chloride, however, give the *thiourethane*, $NHEt \cdot CS \cdot SBz$, which forms slightly yellow crystals, melts at 76° , and is comparatively stable at the ordinary temperature; when boiled with alcohol, it forms ethylbenzamide.

N-Phenyl-S-benzoyldithiourethane crystallises from alcohol, melts at 64° , and is highly coloured; when boiled with alcohol, it forms phenylbenzamide.

Benzoyldithiourethane, $NH_2 \cdot CS \cdot SBz$, obtained from ammonium dithiocarbamate and benzoyl chloride, crystallises from alcohol, melts at $108-109^{\circ}$, and easily affords benzamide.

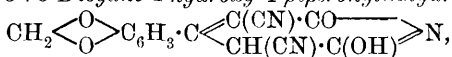
The bright yellow colour of all these substances is emphasised, and its relationship with that shown by other sulphur compounds (*Abstr.*, 1903, i, 618—619) discussed.
W. A. D.

Action of Chloralammonia on Ethyl Disodiummalonate. RUDOLF ZWERGER (*Monatsh.*, 1903, 24, 737—746).—The action of chloralammonia on ethyl disodiummalonate leads to the formation of a substance which is considered to be *diethyl 2:6-dihydroxy-1:4-dihydropyridine-4:4-dicarboxylate*, $\text{NH} \begin{smallmatrix} \text{C}(\text{OH})\cdot\text{CH} \\ \text{C}(\text{OH})\cdot\text{CH} \end{smallmatrix} \text{C}(\text{CO}_2\text{Et})_2$ (compare Guthzeit, Abstr., 1894, i, 71). The ester crystallises in delicate needles containing $\frac{1}{2}\text{H}_2\text{O}$, melts at $195\text{--}196^\circ$, is easily soluble in hot water, absolute alcohol, or ether, and gives an intense red coloration with ferric chloride. The *sodium* derivative, $\text{C}_{11}\text{H}_{14}\text{O}_6\text{NNa}\cdot 2\text{H}_2\text{O}$, crystallises in silky needles and loses $2\text{H}_2\text{O}$ at 105° ; the *barium* derivative, $\text{C}_{22}\text{H}_{28}\text{O}_{12}\text{N}_2\text{Ba}\cdot 2\text{H}_2\text{O}$, forms delicate needles; the *silver* derivative forms a white precipitate of microscopic needles. G. Y.

Condensation of Ethyl Cyanoacetate with Cinnamaldehyde and Piperonaldehyde. GALEAZZO PICCININI (*Atti R. Accad. Torino*, 1903, 38, 894—921. Compare Carrick, Abstr., 1892, 1086, and Guareschi, Abstr., 1900, i, 52, and 1902, i, 819).—The condensation of ethyl cyanoacetate with cinnamaldehyde in presence of ammonia yields: (1) the 2-ammonium derivative of hydrostyryldicyanoglutaconimide [3:5-dicyano-2-hydroxy-4- β -phenylethyldihydro-6-pyridone], $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{C} \begin{smallmatrix} \text{C}(\text{CN})\cdot\text{CO} \\ \text{CH}(\text{CN})\cdot\text{C}(\text{ONH}_4) \end{smallmatrix} \text{N}$, which separates from aqueous alcohol as a white, crystalline mass melting and decomposing at $215\text{--}220^\circ$, and is only decomposed by concentrated hydrochloric acid on heating, when it evolves ammonia; (2) ethyl styrylcynoacrylate, in small quantity.

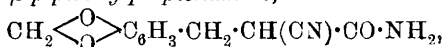
The condensation of ethyl cyanoacetate with piperonaldehyde in presence of ammonia gives:

(1) the *ammonium* derivative of 3:5-dicyano-2-hydroxy-4-piperonyldihydro-6-pyridone, $\text{C}_{14}\text{H}_{10}\text{O}_4\text{N}_4$, which crystallises from aqueous alcohol in long, white needles soluble in water; it is unstable and becomes coloured at the ordinary temperature, evolves ammonia at $70\text{--}80^\circ$, and melts at above 300° . Its aqueous solution gives precipitates with silver nitrate, mercurous nitrate, copper acetate, barium or calcium chloride, &c. 3:5-Dicyano-2-hydroxy-4-piperonyldihydro-6 pyridone,



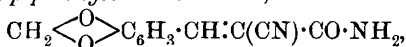
separates from a mixture of alcohol and ether in crystals, which are soluble in aqueous acetone or aqueous acetic acid, become brown at $150\text{--}180^\circ$, and melt at above 300° . The aqueous solution gives precipitates with many inorganic salts, including potassium chloride (1 in 800 solution), and with various alkaloids, including nicotine hydrochloride (a 1 in 16,000 solution is precipitated after a time). The *nicotine* derivative, $\text{C}_{10}\text{H}_4\text{N}_2\cdot 2\text{C}_{14}\text{H}_7\text{O}_4\text{N}_3$, separates in needles which contain $\frac{1}{2}\text{H}_2\text{O}$ and turn brown at 250° , and melt and decompose at about 290° . The derivatives of the following metals were prepared and analysed: *silver*, *barium* (+ $4\text{H}_2\text{O}$), *calcium* (+ $5\text{H}_2\text{O}$), *copper*, and *cobalt*.

(2) α -Cyano- β -piperonylpropionamide,

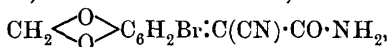


which separates from alcohol in white crystals melting at $186-186.5^\circ$; it has a neutral reaction, and is soluble in water or acetone, showing in the latter a normal ebullioscopic behaviour; when boiled with barium hydroxide in a current of steam, it gives off ammonia (2 mols.).

(3) α -Cyano- β -piperonylideneacetamide,



separating from aqueous alcohol in bright yellow crystals which melt at 209° and evolve ammonia when boiled with barium hydroxide in a current of steam; when treated with bromine, it does not yield an additive product, but a bromo-derivative,



which is deposited from alcohol in slender, yellow crystals, turning brown at 235° and melting at 245° . T. H. P.

Pyridine Bismuth Chloride. OTTO HAUSER and LUDWIG VANINO (*Ber.*, 1903, 36, 3682—3684).—The formula, $2\text{BiCl}_3 \cdot 3\text{C}_5\text{H}_5\text{N}$, previously (*Abstr.*, 1901, i, 289) assigned to the precipitated salt is confirmed (compare Montemartini, *Abstr.*, 1901, i, 163; 1903, i, 111).

J. J. S.

Asymmetric Nitrogen. ALBERT LADENBERG (*Ber.*, 1903, 36, 3694—3699).—The following experiments are adduced to prove the existence of *isostilbazoline*.

l-Stilbazoline *a*-tartrate crystallises in large prisms, not very sharply formed, melting at $78-80^\circ$. At 13° , 100 parts of water dissolve 14.5 parts of the salt. The corresponding base has $[\alpha]_D -9.44^\circ$. By heating stilbazoline, it is converted into a base boiling at $156-158^\circ$ under a pressure of 20 mm. and having $[\alpha]_D -6.3^\circ$ to -6.46° . The tartrate formed from this crystallises easily, and 100 parts of water dissolve about 14 parts. On the other hand, the tartrate prepared from a mixture of the *l*- and *i*-bases, having a specific rotation of about -6.5° , only crystallised after a long interval, and 100 parts of water dissolved more than 50 parts. E. F. A.

Constitution and Optical Behaviour of the Nitrosoalkylurethanes and of Anthranil. JULIUS W. BRÜHL (*Ber.*, 1903, 36, 3634—3645. Compare *Abstr.*, 1902, i, 353).—The refractometric determinations made by O. Schmidt (*Abstr.*, 1903, i, 681) with nitrosoalkylurethanes and anthranil have been repeated by the author, who confirms Schmidt's conclusions as to the constitution of nitrosoalkylurethanes, but agrees with Bamberger, in opposition to Schmidt, as to the constitution of anthranil (compare following abstract).

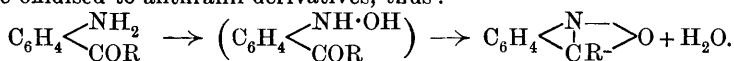
Nitrosoalkylurethanes are true nitrosoamines; the values previously quoted by Brühl (*Abstr.*, 1897, ii, 297) are too high, as the compounds examined were impure. Nitrosoethylurethane boils at 77° under 19 mm. pressure [Schmidt gives $69-70^\circ$ under 15 mm. pressure] $n_D 1.43968$; sp. gr. 1.0885 at $16.9^\circ/4^\circ$; $M_D 35.33$ (Schmidt finds 35.12). Nitrosomethylurethane boils at $67-67.5^\circ$ under 14 mm. pressure; $n_D 1.44196$; sp. gr. 1.1402 at $19^\circ/4^\circ$; $M_D 30.63$

(Schmidt finds 30·66). Since the spectrochemical values for the grouping N_2O in nitrosoalkylamines and nitrosoalkylurethanes (nitrosoacylamines) vary only within the limits of experimental error, the constitution of nitrosoalkylurethanes may be regarded as settled.

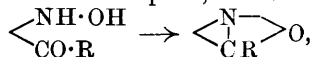
From his optical determinations Schmidt regards anthranil as having the constitution $\text{C}_6\text{H}_4\text{<}\begin{smallmatrix} \text{CO} \\ | \\ \text{NH} \end{smallmatrix}\text{>}$, as against Bamberger's $\text{C}_6\text{H}_4\text{<}\begin{smallmatrix} \text{CH} \\ | \\ \text{N} \end{smallmatrix}\text{>O}$. The author points out that Schmidt's figures do not bear out his conclusion, since the value for the molecular refraction is much smaller than it should be, if the former constitution is correct.

The constitution of methylantranil has been definitely settled by Bamberger, who synthesised it from *o*-nitroacetophenone (Abstr., 1903, i, 432, 560). Comparison of the refractometric values of anthranil and methylantranil indicate the correctness of Bamberger's anthranil formula. Anthranil boils at $93-93\cdot5^\circ$ under 9 mm. pressure; n_D 1·58609; sp. gr. 1·1827 at $19\cdot8^\circ/4^\circ$; M_D 33·77 (calculated = 33·156). Methylantranil boils at $115\cdot5-116^\circ$ under 11 mm. pressure; n_D 1·57967; sp. gr. 1·1334 at $19\cdot95^\circ/4^\circ$; M_D 39·04 (calculated = 37·759). A. McK.

Anthranil. VIII. EUGEN BAMBERGER and FRANZ ELGER (*Ber.*, 1903, 36, 3645—3658. Compare Abstr., 1902, i, 127, 95, 650; 1903, i, 84, 432, 417, 560; also preceding abstract).—Bamberger and his pupils have shown that *o*-amino-aromatic aldehydes and ketones can be oxidised to anthranil derivatives, thus:



This is not, however, a general reaction for substances of the type $\text{C}_6\text{H}_4(\text{NH}_2)\text{COR}$, since anthranilic acid (or methyl anthranilate) is oxidised by Caro's acid to *o*-nitrosobenzoic acid (or methyl *o*-nitrosobenzoate) and not to hydroxyanthranil (or methoxyanthranil). If the intramolecular dehydration of the hypothetical intermediate hydroxylamine derivative takes place, thus:



more quickly than its oxidation, thus: $\text{<}\begin{smallmatrix} \text{NH}\cdot\text{OH} \\ | \\ \text{CO}\cdot\text{R} \end{smallmatrix}\text{>} \rightarrow \text{<}\begin{smallmatrix} \text{NO} \\ | \\ \text{CO}\cdot\text{R} \end{smallmatrix}\text{>}$, then an anthranil is formed; if the oxidation takes place more rapidly than the dehydration, a nitroso-compound is obtained.

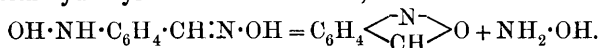
It is now shown that *o*-nitrobenzaldehydedimethylacetal, *o*-nitrobenzaldehyde, and *o*-nitroacetophenone, when carefully reduced, can be converted into the corresponding hydroxylamine derivatives, which, in the presence of hydrogen ions, undergo transformation with such extreme ease into anthranils that it was found impossible to isolate them. *o*-Aminoacetophenone and *o*-aminobenzophenone, when oxidised by Caro's acid, yield methylantranil and phenylantranil respectively.

When *o*-nitrobenzaldehydedimethylacetal, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OMe})_2$, is reduced by aluminium amalgam, it forms *o*-hydroxylaminobenzaldehyde dimethylacetal, $\text{OH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OMe})_2$, the aqueous solution of which quickly becomes turbid on exposure to air (in the same manner as

an aqueous solution of phenylhydroxylamine), reduces Fehling's solution in the cold, and interacts with diazonium chloride to form a substance giving the ferric chloride coloration characteristic of benzeneazohydroxylanilide. Addition of a drop of dilute hydrochloric acid to the aqueous solution of this hydroxylamine compound causes the immediate formation of anthranil. The reduction of *o*-nitrobenzaldehydediethylacetal by ammonium chloride and zinc dust proceeds in an analogous manner.

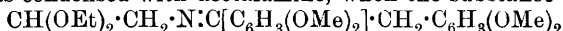
When *o*-nitrobenzaldehyde is reduced by aluminium amalgam, it yields anthranil with the intermediate formation of *o*-hydroxylaminobenzaldehyde. Similarly, *o*-nitroacetophenone yields methylantranil with the intermediate formation of *o*-hydroxylaminoacetophenone, which was detected by its action on Fehling's solution, &c.

By reduction of *o*-nitrobenzaldoxime with ammonium chloride and zinc dust, an almost theoretical yield of *o*-hydroxylaminobenzaldoxime may be obtained (compare Bamberger and Demuth, Abstr., 1902, i, 95). The latter is oxidised by a current of air to *o*-azoxybenzaldoxime, $\text{ON}_2(\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{OH})_2$, and anthranil; dilute acid also decomposes it to form hydroxylamine and anthranil, thus:



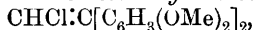
A. McK.

Syntheses in the isoQuinoline Series. II. Attempts to Synthesise Papaverine. PAUL FRITSCH (*Annalen*, 1903, 329, 37—65. Compare Abstr., 1895, i, 624).—Starting from 3:4:3':4'-tetramethoxydeoxybenzoin, the synthesis of papaverine has been attempted; this compound was condensed with acetalamine, when the substance



was formed, which yielded a very small quantity of an alkaloid isomeric with papaverine; the melting point, however, was considerably higher than that of papaverine.

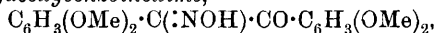
Diveratryldichloroethane, $\text{CHCl}_2\cdot\text{CH}[\text{C}_6\text{H}_3(\text{OMe})_2]_2$, is prepared by condensing veratrole with dichloroacetal by means of 72.5 per cent. sulphuric acid; the product is poured on to ice and the solid which separates after treatment with water and cold alcohol, dissolved in warm alcohol, whence the condensation product separates in lustrous prisms melting at 122°; on treatment with alcoholic potassium hydroxide, it is converted into *diveratrylchloroethylene*,



which crystallises in colourless needles melting at 98° and is soluble in sulphuric acid with an intense reddish-violet coloration. *Tetramethoxytolane*, $\text{C}_2[\text{C}_6\text{H}_3(\text{OMe})_2]_2$, is obtained from this compound by heating it under pressure with a solution of potassium in amyl alcohol for 2 hours at 175—180°; from the solid product of the reaction, the unchanged material was extracted by means of ether, in which the tolane is but little soluble; the tolane, the yield of which never exceeds 45 per cent. of the theoretical, crystallises in colourless prisms melting at 156°, and dissolves in sulphuric acid with an intense violet coloration. The *dibromide*, $\text{C}_2\text{Br}_2[\text{C}_6\text{H}_3(\text{OMe})_2]_2$, crystallises in leaflets melting at 208°.

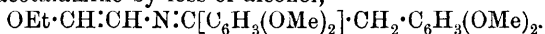
Many attempts were made to prepare the tetramethoxydeoxybenzoin from the tolane derivative; it was finally obtained by dissolving the tolane in mercaptan saturated with hydrogen chloride and treating the product thus formed with ether and hydrogen chloride; the deoxybenzoin crystallises from alcohol in needles melting at 108° and is soluble in sulphuric acid, no coloration appearing. The mercaptol, $C_6H_3(OMe)_2 \cdot C(SET):CH \cdot C_6H_3(OMe)_2$, is doubtless formed as an intermediate product and can be isolated under certain conditions; it is an oil boiling at $190-200^{\circ}$ under 15 mm. pressure.

Tetramethoxydeoxybenzoinoxime,



is prepared by adding an alcoholic solution of sodium containing amyl nitrite to a solution of the deoxybenzoin in benzene, and then extracting the solution with dilute alkali hydroxide; it crystallises in colourless leaflets melting at $149-150^{\circ}$. *Tetramethoxybenzil* was obtained from the last mentioned compound by treating its solution in acetic acid with sodium nitrite, and crystallises in yellow needles or prisms melting at $219-220^{\circ}$. This substance was also prepared from the dimethyl ether of vanillin by treatment of its alcoholic solution with potassium cyanide and subsequent oxidation of the benzoin, which was not isolated, with ammoniacal copper oxide. The identity of the two substances demonstrates the correctness of the constitution of tetramethoxydeoxybenzoin, above given.

Tetramethoxydeoxybenzoinacetalamine is prepared by slowly adding acetalamine to the deoxybenzoin, which is heated in a special apparatus in a stream of dry hydrogen at $200-210^{\circ}$; it is a viscous, yellowish-brown oil, and is immediately decomposed into its constituents by water. When distilled under a pressure of 0.35 mm., a red oil passes over at $255-265^{\circ}$, which is probably a vinyl derivative, formed from the acetalamine by loss of alcohol,



Since papaverine can be recovered without loss from a solution in 80 per cent. sulphuric acid, whilst only about 30 per cent. can be recovered from a solution in 85 per cent. sulphuric acid, the conversion of the acetalamine derivative into the alkaloid was attempted by treatment with 75 per cent. sulphuric acid; a base, $C_{20}H_{21}O_4N$, was obtained which crystallised in pale yellow leaflets melting at 162° (papaverine melts at 147°), but resembling the alkaloid in other respects.

The author discusses the syntheses in the *isoquinoline* series in the light of the recent work of Rügheimer (Abstr., 1903, i, 438).

K. J. P. O.

The Acetylenic Ketones. New Method of Synthesising isoOxazoles. CHARLES MOUREU and M. BRACHIN (*Compt. rend.*, 1903, 137, 795—797).—By the action of hydroxylamine on acetylphenylacetylene, $(CPh:C \cdot COMe)$, in aqueous alcoholic solution, 5-phenyl-3-methylisooxazole, $O < \begin{matrix} N=CHMe \\ | \\ CPh:CH \end{matrix}$, is formed; it melts at 68° (Goldschmidt, Abstr., 1895, i, 529, gives 65°) and boils at $151-152^{\circ}$ under 19 mm. pressure.

Propionylphenylacetylene, $CPh:C:C \cdot COEt$, prepared by the action of

propionyl chloride on the sodium derivative of phenylacetylene, boils at 137—138° under 16 mm. pressure, melts at 8—10°, has a sp. gr. 1·0043 at 23°/0°, and on treatment with hydroxylamine yields

5-phenyl-3-ethylisooxazole, $\text{O} \begin{array}{c} \text{N}=\text{C}^{\text{Et}} \\ | \\ \text{CPh}:\text{CH} \end{array}$, which boils at 157—158° under 18 mm. pressure, melts at about -2°, and has a sp. gr. 1·0766 at 18°/0°; it dissolves in concentrated hydrochloric acid and is reprecipitated by water.

Butyrylphenylacetylene, $\text{CPh}:\text{C}:\text{C}\cdot\text{COPr}$, obtained by the condensation of the sodium derivative of phenylacetylene and butyryl chloride, boils at 148—150° under 18 mm. pressure, and has a sp. gr. 0·9859 at 23°/0°; it reacts with hydroxylamine to form 5-phenyl-3-propylisooxazole, $\text{O} \begin{array}{c} \text{N}=\text{C}^{\text{Pr}} \\ | \\ \text{CPh}:\text{CH} \end{array}$, which boils at 168—169° under 18 mm. pressure, melts between 5° and 10°, and has a sp. gr. 1·0536 at 18°/0°; it dissolves in concentrated hydrochloric acid and is reprecipitated by water.

3:5-Diphenylisooxazole, $\text{O} \begin{array}{c} \text{N}=\text{C}^{\text{Ph}} \\ | \\ \text{CPh}:\text{CH} \end{array}$, formed from benzoylphenylacetylene, crystallises from alcohol, is slightly soluble in ether, and insoluble in concentrated hydrochloric acid. It melts between 142° and 190°, giving off a gas at 170°; the resolidified product melts between 140° and 146° (Goldschmidt, Abstr., 1896, i, 189, gives 141° as the melting point of this compound).

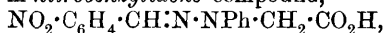
3-Anisyl-5-phenylisooxazole, $\text{O} \begin{array}{c} \text{N}=\text{C}^{\text{C}_6\text{H}_4\cdot\text{OMe}} \\ | \\ \text{CPh}:\text{CH} \end{array}$, formed from anisoylphenylacetylene and hydroxylamine, crystallises from methyl alcohol in thin, white needles, melts at 128—129°, and is insoluble in concentrated hydrochloric acid.

The formation of these isooxazoles takes place in two phases, (1) $\text{CPh}:\text{C}\cdot\text{COMe} + \text{NH}_2\cdot\text{OH} = \text{H}_2\text{O} + \text{CPh}:\text{C}\cdot\text{CMe}:\text{N}\cdot\text{OH}$, and (2) the acetylenic oxime changes into the isomeric isooxazole, $\text{O} \begin{array}{c} \text{N}=\text{C}^{\text{Me}} \\ | \\ \text{CPh}:\text{CH} \end{array}$
M. A. W.

Diacid Quaternary Ammonium Bases: Ethylenedikairolinium Iodide. EDGAR WEDEKIND (*Ber.*, 1903, 36, 3796—3801. Compare Abstr., 1903, i, 517).—Kairolin and ethylene iodide unite to form a tertiary compound, the hydriodide of 1-methyltetrahydroquinoline, decomposing at 164—165°, as chief product, as well as small quantities of a quaternary iodide melting at 265—266°. *Ethyleneditetrahydroquinoline*, $\text{C}_9\text{NH}_{10}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_9\text{NH}_{10}$, prepared by heating a mixture of tetrahydroquinoline (4 mols.) and ethylene bromide (1 mol.) at 100°, crystallises from alcohol in colourless needles melting at 146—147°. Heating with an excess of methyl iodide converts this into *ethylenedikairolinium iodide*, $\text{C}_2\text{H}_4(\text{C}_9\text{NH}_{10}\text{MeI})_2$, which forms colourless needles melting and decomposing at 206°; it is therefore probably isomeric with the quaternary iodide just described. The *d-camphorsulphonate* forms colourless crystals which melt at a higher temperature than the iodide does.
E. F. A.

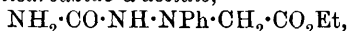
The Two Phenylhydrazinoacetic Acids. MAX BUSCH, SEBASTIAN SCHNEIDER, and AUGUST WALTER (*Ber.*, 1903, **36**, 3877—3890. Compare Elbers, *Abstr.*, 1885, 534; Reissert and Kayser, 1891, 1054; Reissert, 1895, i, 460; Harries, *ibid.*, 459).—A mixture of the ethyl esters of *s*- and *as*-phenylhydrazinoacetic acids is obtained by the condensation of ethyl chloroacetate and phenylhydrazine by Reissert's method. When the condensation takes place between the acid and phenylhydrazine in the presence of an alkali hydroxide, the only product is Harries' *as*-phenylhydrazinoacetic acid. The two isomeric acids may be separated by the addition of an aqueous solution of oxalic acid, the *s*-acid remains undissolved as it is less basic, whereas the *as*-acid forms a soluble oxalate. *s*-Phenylhydrazinoacetic acid, $\text{NHPh}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, crystallises in colourless, glistening plates, begins to turn brown at 170° , and melts and decomposes at 172 — 173° . It is only sparingly soluble in alcohol or water and is practically insoluble in ether or benzene. On treatment with ammoniacal copper solutions, it yields the phenylhydrazone of glyoxylic acid and no nitrogen is evolved. The *hydrochloride* of the hydrazino-acid melts and decomposes at about 165° , the hydrochloride of the ester has only been obtained as an oil. The *oxalate* of the ester may be obtained by the addition of an ethereal solution of the ester to a solution of oxalic acid in the same solvent.

as-Phenylhydrazinoacetic acid yields a hydrochloride melting and decomposing at about 170° , a benzylidene derivative melting at 165 — 166° , and a *m*-nitrobenzylidene compound,



melting at 196 — 197° . The hydrochloride of the ethyl ester may be obtained by passing hydrogen chloride into an alcoholic solution of the acid and is readily soluble in warm water (compare Harries.) The corresponding *oxalate* melts at 126° and is readily soluble in cold water, and the *m*-nitrobenzylidene derivative crystallises in small yellow needles and melts at 86° .

Ethyl α -phenylsemicarbazido- α -acetate,



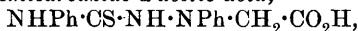
obtained by the action of potassium cyanate on an aqueous solution of the ethyl ester of the *as*-acid, crystallises from hot water in compact crystals melting at 123° and readily soluble in alcohol. On hydrolysis with aqueous sodium hydroxide, it yields *α -phenylsemicarbazido- α -acetic acid*, melting at 190 — 191° , but with alcoholic potash yields *phenyldiketohexahydro-1 : 2 : 4-triazine*, $\text{NPh}\langle\begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \text{CH}_2\cdot\text{CO} \end{smallmatrix}\rangle\text{NH}$, which crystallises from hot water in iridescent, thin plates melting at 225° . It has the properties of a feeble acid and dissolves in sodium hydroxide solution, but not in ammonia. When boiled with alkali, the ring is ruptured and the phenylcarbazidoacetic acid is formed.

Ethyl cyanate and ethyl *as*-phenylhydrazinoacetate yield *ethyl α -phenyl- δ -ethylsemicarbazido- α -acetate*, $\text{NHEt}\cdot\text{CO}\cdot\text{NH}\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, which forms transparent, flat prisms melting at 97 — 98° . The corresponding acid melts at 195° , and *1-phenyl-4-ethyldiketohexahydro-1 : 2 : 4-triazine* at 135 — 136° .

Ethyl α,δ -diphenylsemicarbazido- α -acetate forms small, colourless

needles, readily soluble in alcohol or benzene and melting at 160° , the corresponding *acid* crystallises in either needles or plates melting and decomposing at $203\text{--}204^{\circ}$. A triazine derivative has not been obtained.

ad-Diphenylthiosemicarbazide-a-acetic acid,



obtained from the ethyl ester (compare Harries, *loc. cit.*), crystallises in colourless needles and melts and decomposes at 195° . When the ethyl ester is digested with cold alcoholic potash, a mixture of the free acid and of a yellow compound, $\text{NPh}\cdot\text{C}\begin{smallmatrix} \text{NH}\cdot\text{NPh} \\ \text{S} \text{---} \text{CO} \end{smallmatrix} \text{CH}_2$, melting and decomposing at 201° is obtained. This yellow compound may readily be separated from the acid, as it is insoluble in sodium carbonate solution. It is also sparingly soluble in the ordinary solvents. Carbonyl chloride reacts with ethyl *as*-phenylhydrazinoacetate yielding an oil, $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{NPh}\cdot\text{NH}\cdot\text{COCl}$, and *ethyl diphenylcarbazidodiacetate*, $\text{CO}(\text{NH}\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_2$, in the form of colourless prisms softening at $114\text{--}115^{\circ}$ and decomposing at a higher temperature. The *acid* melts and decomposes at 235° and is only sparingly soluble in alcohol or glacial acetic acid. The ester, on treatment with cold alcoholic potash yields a soluble *acid*, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{NPh}\cdot\text{N}\begin{smallmatrix} \text{CO}\cdot\text{CH}_2 \\ \text{CO}\cdot\text{NH} \end{smallmatrix} \text{NPh}$, melting at 176° , together with the acid melting at 235° . J. J. S.

Hydrazones derived from *p*-Nitrophenylhydrazine and *p*-Dinitrodibenzylhydrazine. WILLIAM ALBERDA VAN EKENSTEIN and JAN J. BLANKSMA (*Rec. trav. chim.*, 1903, 22, 434—439. Compare Bamberger and Kraus, *Abstr.*, 1896, i, 610; 1899, i, 666, and Hyde, *Abstr.*, 1899, i, 688).—When dextrose (2 grams) dissolved in alcohol (30 c.c.) is warmed for ten minutes at 100° with *p*-nitrophenylhydrazine (2 grams) and the liquid evaporated to dryness in a desiccator, there is formed a *dextrose-p-nitrophenylhydrazone*, which crystallises in yellow needles, melts at 185° , and has $[\alpha]_D + 21.5^{\circ}$ in pyridine. When acetic acid is employed as the solvent, there is formed a second *dextrose-p-nitrophenylhydrazone*, which separates from alcohol in yellow crystals, melts at 195° , and has $[\alpha]_D - 128.7^{\circ}$. This modification is also produced by solution of the form melting at 185° in acetic acid. From both forms, the same osazone is readily obtained by the further action of *p*-nitrophenylhydrazine in presence of acetic acid (Hyde, *loc. cit.*).

Mannose-p-nitrophenylhydrazone, similarly prepared, also exists in two forms, the one (produced in presence of methyl alcohol) forming yellow crystals and melting at 190° , the other (produced in presence of acetic acid) melting at 202° .

The following *p*-nitrophenylhydrazones of other sugars have been prepared: *laevulose-p-nitrophenylhydrazone* melts at 176° and has $[\alpha]_D + 16^{\circ}$; *galactose-p-nitrophenylhydrazone* melts at 192° and has $[\alpha]_D + 45.6^{\circ}$; *xylose-p-nitrophenylhydrazone* melts at 156° , *ribose-p-nitrophenylhydrazone* melts at 186° and has $[\alpha]_D + 48.3^{\circ}$, whilst *arabinose-p-nitrophenylhydrazone* melts at 168° and has $[\alpha]_D + 48.3^{\circ}$. Maltose and lactose do not react with *p*-nitrophenylhydrazine in presence of alcohol.

From these *p*-nitrophenylhydrazones, the sugars are readily regenerated by warming with benzaldehyde, when the *p*-nitrophenylhydrazone of the latter is formed, melting at 190° (compare Hyde, *loc. cit.*). The corresponding *derivatives* of *o*-nitrobenzaldehyde, *p*-tolualdehyde, and salicylaldehyde melt respectively at 250°, 198°, and 225°.

The author has also prepared the *p*-dinitrodibenzylhydrazones of the following substances; the melting points of these are given in brackets: dextrose (142°), galactose (153°), lævulose (112°), *o*-nitrobenzaldehyde (120°), *p*-tolualdehyde (163°), and salicylaldehyde (183°).

It is suggested that *p*-nitrophenylhydrazine may be employed for the detection of acetone in alcohol denatured with wood spirit, and in urine. Diethyl ketone and methyl ethyl ketone, which may also occur in wood spirit, furnish *p*-nitrophenylhydrazones, melting respectively at 141° and 128°.

T. A. H.

Action of Iodine on Benzaldehydephenylhydrazone in Pyridine Solution. GIOVANNI ORTOLEVA (*Gazzetta*, 1903, 33, ii, 51—60).—The action of iodine on benzaldehydephenylhydrazone in pyridine solution results in the formation of: (1) diphenyldibenzylidenehydrotetrazone, (2) dehydrobenzaldehydephenylhydrazone, and (3) a compound, $C_{18}H_{18}N_3I$, which crystallises from alcohol in yellow needles melting at 265—267°, and is soluble in water, acetic acid, acetic anhydride, or dilute hydrochloric acid, from the last two of which it separates unchanged after boiling; when boiled with alkalis, it is completely resinified and evolves a basic odour similar to that of pyridine; from its aqueous solution, silver nitrate completely precipitates the iodine, whilst with mercuric chloride it gives a double salt, $C_{18}H_{18}N_3I \cdot 3HgCl_2 \cdot H_2O$, which separates from water in white needles melting at 202—204°; when heated with dilute nitric acid, it yields a base, which separates from a mixture of chloroform and ether in slender, white needles melting at 214—215° and yields, with mercuric chloride, a compound separating from water in white needles melting at 219—220°, whilst its *platinichloride*, $(C_{18}H_{17}N_3)_2 \cdot H_2PtCl_6$, melts and decomposes at 238—239°; the same *platinichloride* is obtained from the original compound, $C_{18}H_{18}N_3I$, and from the compound obtained by the action of dilute hydrochloric acid on the latter.

T. H. P.

Condensation of Oximes with Hydrazines and the Properties of Hydrazones. CHARLES REUTT and BRONISLAS PAWLEWSKI (*Bull. Acad. Sci. Cracow*, 1903, 502—504).—The authors have attempted to prepare compounds of the type $R \cdot CH:N \cdot NH \cdot NHR'$ by condensing aldoximes with hydrazines, but have obtained instead the corresponding hydrazones of the aldehydes (compare Just, *Abstr.*, 1886, 701).

Benzaldehydephenylhydrazone, produced by the condensation of benzaldoxime with phenylhydrazine, melts at 158—160° and decomposes when heated at 100—110°. The red *modification* produced by the exposure of this to light melts at the same temperature and is reconverted into the colourless form at 115—120° or by preservation in the dark.

Benzaldehyde-o-tolylhydrazone, $CHPh \cdot N \cdot NH \cdot C_6H_4Me$, produced in small quantity by condensing benzaldoxime with *o*-tolylhydrazine,

forms golden-yellow needles, melts at 100—102°, and is converted by the action of light into a red form which melts at 80—83°.

Benzaldehyde-p-tolylhydrazone, similarly prepared, forms short, sand-coloured needles, melts at 114°, and becomes red on exposure to light, the melting point falling at the same time to 101°. T. A. H.

Action of Phenylcarbimide on Amino-acids. CARL PAAL and GEORG ZITELMANN (*Ber.*, 1903, 36, 3337—3345).—*Phenylureidosuccinic monoamide*, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, formed by the addition of phenylcarbimide to a solution of *l*-asparagine in sodium hydroxide, forms colourless prisms and melts at 164°. It is dextro-rotatory, having $[\alpha]_D + 21.66^\circ$ at 16°, where $p = 8.7$ and $d = 1.040$. Its *barium* and *silver* salts are described.

By the action of phenylcarbimide on a solution of *l*-aspartic acid in sodium hydroxide, a mixture of phenylureidosuccinic acid and its anhydride, γ -phenylhydantoin- α -acetic acid, is formed. When this mixture is heated with dilute sodium hydroxide solution or with baryta water and the resulting solution then acidified by hydrochloric acid, *phenylureidosuccinic acid*, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, separates in colourless crystals which melt at 183°. It may also be formed from phenylureidosuccinic monoamide or from γ -phenylhydantoin- α -acetic acid. It has $[\alpha]_D + 5.70^\circ$ at 16°, where $p = 10.82$ and $d = 1.069$. Its *barium* and *silver* salts are described. The acid very readily parts with water to form γ -phenylhydantoin- α -acetic acid, $\text{CO} < \begin{matrix} \text{NPh}\cdot\text{CO} \\ | \\ \text{NH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H} \end{matrix}$, which may also be formed by heating phenylureidosuccinic monoamide with hydrochloric acid. It crystallises from water in colourless prisms or needles which melt at 228°; its *sodium* salt has $[\alpha]_D - 52.05^\circ$ at 16°, where $p = 8.52$ and $d = 1.043$. Its *ethyl* ester separates from alcohol in colourless leaflets and melts at 122°.

2-Phenylureidoethanesulphonic acid, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$, prepared from phenylcarbimide and taurine, separates in colourless, tiny needles and decomposes at 175°. Its *barium* salt crystallises with $1\frac{1}{2}\text{H}_2\text{O}$. The acid does not form an anhydride when heated with hydrochloric acid, acetic anhydride, or acetyl chloride.

β -*p*-Hydroxyphenyl- α -phenylureidopropionic acid,

$\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, $\frac{1}{2}\text{H}_2\text{O}$, prepared from phenylcarbimide and tyrosine, melts at 104°. Its *barium* salt contains $6\text{H}_2\text{O}$ and its *silver* salt $1\text{H}_2\text{O}$. When warmed with dilute sulphuric acid, the acid forms α -*p*-hydroxybenzyl- γ -phenylhydantoin, $\text{CO} < \begin{matrix} \text{NPh}\cdot\text{CO} \\ | \\ \text{NH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH} \end{matrix}$, which separates from water in colourless needles and melts at 184°. A. McK.

Chrysean. GUSTAF HELLSING (*Ber.*, 1903, 36, 3546—3553. Compare Abstr., 1899, i, 563; 1900, i, 518).—The following facts show that chrysean is either 4-aminothiazole-2-carbothioamide, $\text{S} < \begin{matrix} \text{CH}=\text{C}\cdot\text{NH}_2 \\ | \\ \text{C}(\text{CS}\cdot\text{NH}_2)\cdot\text{N} \end{matrix}$, or the corresponding μ -aminoisothiazole- α -carbothioamide.

Chrysean methiodide, $C_4H_5N_3S_2$, obtained by interaction of chrysean with methyl iodide in alcoholic solution, crystallises from alcohol in slender, yellowish-brown needles, and commences to decompose at 180° . The *formyl* derivative, $C_4H_3N_2S_2 \cdot NH \cdot CHO$, prepared by boiling chrysean with anhydrous formic acid, crystallises from alcohol in golden spangles and decomposes at 210° . The *benzoyl* derivative, $C_4H_3N_2S_2 \cdot NHBz$, forms small, yellowish-brown needles and melts at $212-213^\circ$.

The substance melting at 216° , which was previously described (*loc. cit.*) as 1-acetyl-4:4-dimethyl-2:6-dicyanodihydrodithiazine, is in reality the *diacetyl* derivative, $S \begin{smallmatrix} \text{CH}=\text{C} \cdot NAc_2 \\ \text{C}(CS \cdot NH_2):N \end{smallmatrix}$, of chrysean, and can be obtained by boiling this substance with acetic anhydride alone. The compound formed by heating chrysean with aqueous silver sulphate is, moreover, not a dicyanodihydroazthiotetride, but *aminocyanothiazole*, $S \begin{smallmatrix} \text{CH}=\text{C} \cdot NH_2 \\ \text{C}(CN):N \end{smallmatrix}$; with benzaldehyde, it gives the

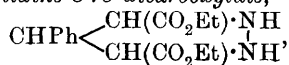
benzylidene derivative, $CN \cdot C_3NSH \cdot N \cdot CHPh$, which crystallises from alcohol in small, yellowish-white needles and melts at $140-141^\circ$.

Acetylaminothiazolecarboxylamide, $NHAc \cdot C_3NSH \cdot CO \cdot NH_2$, prepared by the action of hydrogen peroxide on the corresponding nitrile ("acetyldicyanodihydroazthiotetride"), crystallises in small, six-sided plates and decomposes above 250° ; *acetylaminothiazolecarboxylic acid*, $NHAc \cdot C_3NSH \cdot CO_2H$, obtained by hydrolysing the amide, melts and decomposes at 166° , and gives a *sodium* salt crystallising in white needles and a *methyl* ester which melts and decomposes at 178° . *Acetylaminothiazole*, $C_3NSH_2 \cdot NHAc$, prepared by decomposing the carboxylic acid at $170-180^\circ$, crystallises from alcohol, benzene, or water both with and without solvent of crystallisation and melts at 162° .

When aminocyanothiazole and its acetyl derivative are caused to combine with hydrogen sulphide in alcoholic solution, they give rise respectively to chrysean and acetylchrysean. W. A. D.

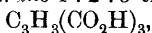
Reduced Derivatives of 4-Phenylpyrazole. *cis*-1-Phenyl-*trans*-2:3-trimethylenedicarboxylic Acid. EDWARD BUCHNER and LASAR PERKEL (*Ber.*, 1903, 36, 3774-3782).—4-*Phenylpyrazoline*, $NH \begin{smallmatrix} N=CH \\ | \\ CH_2 \cdot CHPh \end{smallmatrix}$, prepared by heating ethyl 4-phenylpyrazolinedicarboxylate (from ethyl cinnamate and ethyl diazoacetate) with hydrochloric acid, is an oil which oxidises very readily in air to phenylpyrazole. It does not lose nitrogen when heated at $230-240^\circ$, but is partially converted into 4-phenylpyrazole and hydrogen. The hydrochloride melting at 162° has already been described (*Abstr.*, 1893, i, 282), the *platinichloride* is very unstable and melts at $116-117^\circ$. The *aurichloride* is a yellow precipitate which decomposes without melting when heated. The *oxalate* separates from alcohol in white crystals and melts at 120° .

Ethyl 4-phenylpyrazolidine-3:5-dicarboxylate,



prepared by reducing the pyrazoline ester with zinc dust and acetic acid, boils at 280° without decomposition, crystallises from ether in colourless needles, and melts at 91° . The *acid* crystallises from boiling water in colourless needles, melts at $227-228^{\circ}$, does not immediately decolorise alkaline permanganate, is not acted on by bromine, and does not lose carbon dioxide when heated with hydrochloric acid; the benzyl derivative crystallises from alcohol and melts and decomposes at 280° , but it was not analysed.

The *nitro-derivative*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_3\text{H}_3(\text{CO}_2\text{H})_2$, of *cis*-1-phenyl-*trans*-2:3-trimethylenedicarboxylic acid (Abstr., 1892, 849) separates from water in colourless needles and melts with slight decomposition at 245° . The *amino-derivative*, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_3\text{H}_3(\text{CO}_2\text{H})_2$, forms colourless crystals which become brown at 220° , but do not melt at 300° ; the *hydrochloride* forms colourless needles and melts and decomposes at 198° ; the *hydrochloride* of the *dimethyl ester* crystallises from methyl alcohol and melts and decomposes at 204° . The amino-derivative is oxidised by permanganate to trimethylene-*trans*-1:2:3-tricarboxylic acid,



thus establishing the position of the phenyl group; the relative positions of the two carboxyl groups in the phenyl compound had already been determined by conversion into an anhydride. An isomeric acid, probably *cis*-1-phenyltrimethylene-*cis-trans*-2:3-dicarboxylic acid is produced by fusing the *trans*-acid with potassium hydroxide at $230-240^{\circ}$; it separates from boiling water in colourless needles, melts at 121° , and is stable towards aqueous permanganate.

T. M. L.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. ROBERT STOLLÉ (*J. pr. Chem.*, 1903, [ii], 68, 417—424. Compare Abstr., 1903, i, 721).—The action of acid chlorides on the silver derivatives of the condensation products of aldehydes or ketones with acylhydrazides leads to the formation of additive compounds (Minunni and Satta, Abstr., 1900, i, 251), which by elimination of silver chloride pass over into substituted dihydrodiazoles.

By this reaction, there have been prepared 4-benzoyl-2:5-diphenyl-4:5-dihydro-1:2:4-oxadiazole, $\text{N} \begin{smallmatrix} \nearrow \text{NBz} \cdot \text{CHPh} \\ \searrow \text{CPh} \cdot \text{O} \end{smallmatrix}$, from the silver derivative of benzylidenebenzhydrazone and benzoic chloride; 4-acetyl-2:5-diphenyl-4:5-dihydro-1:2:4-oxadiazole, which melts at 53° , from benzylidenebenzhydrazone and acetic chloride; 4-benzoyl-5-phenyl-2-methyl-4:5-dihydro-1:2:4-oxadiazole, which melts at 98° , from benzylideneacethydrazone and benzoic chloride; 4-acetyl-5-phenyl-2-methyl-4:5-dihydro-1:2:4-oxadiazole, from benzylideneacethydrazone and acetic chloride; and 4-benzoyl-2:5:5-triphenyl-4:5-dihydro-1:2:4-oxadiazole, from benzophenonebenzhydrazone and benzoic chloride.

These dihydro-oxadiazoles are crystalline, stable solids and are easily soluble in alcohol, but less so in ether. When boiled with a few drops of hydrochloric acid in ethereal solution, they are hydrolysed with formation of diacylhydrazides, but in aqueous solution with formation of the products of hydrolysis of these.

G. Y.

Derivatives of Pyrimidine and Methylated Pyrimidines. SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1903, **36**, 3379—3385. Compare Büttner, this vol., i, 658).—The chlorodimethoxypyrimidine, melting at 73°, described by Büttner is reduced by zinc dust and fuming hydrochloric acid in alcoholic solution to a 2:6-dimethoxypyrimidine, which boils at 204·5—205°, solidifies at 10°, is miscible with water, gives a white, crystalline double salt, $2C_6H_8O_2N_2 \cdot 3HgCl_2$, with mercuric chloride, and forms an *aurichloride*, $C_6H_8O_2N_2 \cdot HAuCl_4$, melting at 139·5°. When heated on the water-bath with strong hydrochloric acid, it is converted into uracil, thus establishing its constitution, as also that of Büttner's compound, as 4-chloro-2:6-dimethoxypyrimidine.

4-Chloro-2-amino-6-methoxypyrimidine, which melts at 168—169°, can be obtained either from 4:6-dichloro-2-aminopyrimidine by heating it with methyl alcohol and sodium or by acting on Büttner's dichloromethoxypyrimidine, melting at 51°, with methyl-alcoholic ammonia. Büttner's base is therefore 2:4-dichloro-6-methoxypyrimidine.

2-Amino-6-methoxypyrimidine, formed by reducing the above substance, boils at 274°, crystallises from ethyl acetate in quadratic plates melting at 118·5—120°, is soluble in warm water with an alkaline reaction, and forms a *platinichloride*, $(C_5H_7ON_3)_2 \cdot H_2PtCl_6$, which sinters at 236° but is not melted at 270°. 2-Amino-6-hydroxypyrimidine, prepared by evaporating the preceding base with concentrated hydrochloric acid, crystallises in microscopic cubes and octahedra melting at 276—277°, and is identical with the base prepared synthetically by Wheeler and Johnson (*Abstr.*, 1903, i, 526). 6-Chloro-2-aminopyrimidine is formed when the preceding compound is boiled with phosphorus oxychloride; it sinters and becomes brown at 168°.

4-Methylpyrimidine condenses with benzaldehyde in presence of zinc chloride to form 4-styrylpyrimidine, $N \begin{smallmatrix} \text{CH:CH} \\ \text{CH—N} \end{smallmatrix} > C \cdot CH:CHPh$, which boils at 325—327°, crystallises from light petroleum in plates melting at 72—74°, and forms a *dibromide*, $C_{12}H_{10}N_2Br_2$, crystallising from alcohol in brownish-yellow, oblong plates, which melt and decompose at 225—226°. 2:4-Dimethylpyrimidine condenses with benzaldehyde in similar manner to form 2:4-Distyrylpyrimidine, which crystallises in colourless needles melting at 145—146°. E. F. A.

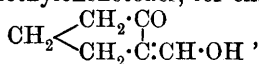
Conversion of Phthalazine into Pyridazine Derivatives. SIEGMUND GABRIEL (*Ber.*, 1903, **36**, 3373—3378).—Chloro-opiazine, $C_6H_2(OMe)_2 \begin{smallmatrix} \text{CH:N} \\ \text{CCl:N} \end{smallmatrix}$, which is best prepared from opiazone by heating it with phosphorus oxychloride, when reduced with hydrogen iodide, has both halogen and methyl replaced by hydrogen, forming 7:8-dihydroxyphthalazine, the *hydrochloride* of which crystallises in yellow needles; the *platinichloride* and the sparingly soluble *picrate* melting at 197° were also prepared. When oxidised with permanganate, this is converted into pyridazine-4:5-dicarboxylic acid, $\begin{smallmatrix} \text{N:CH} \cdot \text{C} \cdot \text{CO}_2\text{H} \\ \text{N:CH} \cdot \text{C} \cdot \text{CO}_2\text{H} \end{smallmatrix}$, which sinters at 205° and melts and decomposes at 212—213·5°; this is

identical with the acid obtained by Täuber on heating pyridazine-tetracarboxylic acid. In a similar manner, phthalazine can be oxidised to the same acid.

4-Iodophthalazine, $C_6H_4 \begin{smallmatrix} \text{CH:N} \\ \text{CI=N} \end{smallmatrix}$, formed by heating 4-chlorophthalazine with hydrogen iodide, crystallises in stellar aggregates of needles and melts at 78° to a reddish-brown mass. E. F. A.

Terpenes and Ethereal Oils. Transformation of Cyclic Ketones into Pyrazole Bases. OTTO WALLACH [with AD. STEINDORFF] (*Annalen*, 1903, 329, 109—133).—With the exception of the preparation of phenylpyrazole from hydroxymethylenecamphor by Claisen, the formation of pyrazoles from cyclic ketones has not been studied. A series of pyrazoles has been obtained in which five-, six-, and seven-membered carbon rings are linked with the simple pyrazole ring. Further unsubstituted pyrazoles, which have not hitherto been prepared, have been obtained.

The cyclic hydroxymethyleneketones, for example,



yield a semicarbazone, which in some instances can be isolated, but generally loses water, forming the compound (carbamide of a pyrazole or cyclic semicarbazone), $CH_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{C} = \text{N} \\ \text{CH}_2 \cdot \text{C} : \text{CH} \end{smallmatrix} > \text{N} \cdot \text{CO} \cdot \text{NH}_2$. On hydrolysis with dilute acids, carbon dioxide and water are eliminated and the pyrazole obtained, $CH_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{C} = \text{N} \\ \text{CH}_2 \cdot \text{C} : \text{CH} \end{smallmatrix} > \text{NH}$. The same pyrazoles can also be obtained directly from the hydroxymethylene compounds by the action of hydrazine, but they cannot be so easily purified when thus prepared.

The carbamide derivatives of the pyrazoles (cyclic semicarbazones) are crystalline insoluble substances, which can be used to recognise the presence of hydroxymethylene compounds.

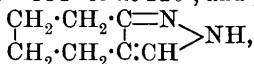
Although two isomeric semicarbazones of a cyclic hydroxymethylene are possible, only one has been observed; the heterocyclic carbamide of the pyrazoles appears to exist in two forms, both of which yield the same pyrazole on hydrolysis, as they exhibit a double melting point in many cases.

The polycyclic pyrazoles are crystalline and very feebly basic; they yield precipitates with mercuric chloride and silver nitrate.

The *hydroxymethylene* derivative of *cyclopentanone* is prepared by adding sodium to a mixture of amyl nitrite and *cyclopentanone*, and forms white crystals melting at 72 — 73° ; it only reacts with semicarbazide in the presence of sulphuric acid, giving a semicarbazone melting at 175 — 177° . When boiled with dilute sulphuric acid, it is converted into a pyrazole which melts at 57 — 59° .

From 1:3-methylcyclopentanone, a *hydroxymethylene* derivative is prepared which melts at 53 — 54° and boils at 105 — 112° under 22 mm. pressure; its cyclic *semicarbazone*, $C_8H_{11}ON_3$, melts at 115 — 116° , and when treated with dilute acids yields an oily pyrazole.

Hydroxymethylenecyclohexanone, prepared from *cyclohexanone*, is an oil boiling at 98—100° under 55 mm. pressure; its cyclic *semicarbazone*, $C_8H_{11}ON_3$, melts at 183—184° or at 220°, and yields the *pyrazole*,



which forms crystals melting at 84°.

The *hydroxymethylene* derivative of 1 : 3-methylcyclohexone is an oil boiling at 85° under 12 mm. pressure, and readily yields a cyclic *semicarbazone*, which melts at 154—157°. The *pyrazole*, $C_8H_{11}N_2$, prepared either from the *semicarbazone* or by the action of hydrazine on the *hydroxymethylene* derivative, melts at 99—100°; the *hydrochloride* is very soluble and the *picrate* is a yellow, crystalline powder melting at 136—138°; the silver nitrate compound, $(C_8H_{12}N_2)_2 \cdot AgNO_3$, crystallises from methyl alcohol and melts at 137—139°.

The *semicarbazone*, $C_{12}H_{21}O_3N_3$, obtained from *hydroxymethylenementhone*, melts at 167—169° and passes into the *carbamide* of the *pyrazole* (cyclic *semicarbazone*), $C_{12}H_{19}ON_3$, which has the melting points 117—118° and 143—144°. The *menthone-pyrazole*, $C_{11}H_{18}N_2$, is an oil and yields a *platinichloride* melting at 216°.

Hydroxymethylenetetrahydrocarvone is a pale yellow liquid boiling at 131—135° under 16 mm. pressure; with *semicarbazide*, it yields the *carbamide* of the *pyrazole*, $C_{12}H_{19}ON_3$, which melts at 150° and not sharply at 178—182°, and is hydrolysed by dilute sulphuric acid to the *pyrazole*, $C_{11}H_{18}N_2$; this base is an oil and gives a *platinichloride* melting at 226—228°.

Hydroxymethylenedihydrocarvone yields a *semicarbazone* melting at 163—165°, which is converted by sulphuric acid into the *carbamide* of the *pyrazole* (the cyclic *semicarbazone*); the latter melts at 125—127° and then solidifies to melt again at 146—148°. The *pyrazole*, $C_{11}H_{16}N_2$, is an oil, the *platinichloride* of which melts at 201°.

Hydroxymethylenethujone reacts with *semicarbazide* in acetic acid solution to form a *monosemicarbazone*, $C_{12}H_{19}O_2N_3$, which melts at 179—181°; it is converted by sulphuric acid in acetic acid solution into the cyclic compound, $C_{12}H_{10}ON_3$, melting at 133—134°. The *pyrazole*, $C_{11}H_{16}N_2$, is an oil and gives a *platinichloride* melting at 188—190°.

Hydroxymethyleneisothujone, which is an oil boiling at 128—132° under 18 mm. pressure, yields a *semicarbazone*, $C_{12}H_{19}O_2N_3$, melting at 204—205°; it readily passes into the cyclic compound, $C_{12}H_{17}ON_3$, melting at 193—194°, with elimination of water. From either by the action of sulphuric acid, the *pyrazole*, $C_{11}H_{16}N_2$, melting at 89—90°, can be prepared; its *platinichloride* melts at 220—222°.

Hydroxymethylenethujamenthone, an oil boiling at 109—115° under 11 mm. pressure, reacts slowly with *semicarbazide*, forming a *semicarbazone*, $C_{12}H_{21}O_2N_3$, which melts at 125—145°; the cyclic compound, $C_{12}H_{19}ON_3$, has a double melting point 121—122°, and 159—161°. The *pyrazole*, $C_{11}H_{18}N_2$, is a liquid.

Hydroxymethylenesuberone, $C_8H_{12}O_2$, is a liquid boiling at 100° under 10 mm. pressure, and when acted on by *semicarbazide* yields directly the cyclic compound, $C_9H_{13}ON_3$, which melts at 181—183°. The

pyrazole, $\text{CH}_2 \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}=\text{N} \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}:\text{CH} \end{array} \text{NH}$, melts at 66—67° and yields a *platinichloride* melting at 238—239°.

Hydroxymethylenecamphor behaves like the compound last mentioned and gives first a *semicarbazone*, $\text{C}_{12}\text{H}_{19}\text{O}_2\text{N}_3$, melting at 217—218°, which then loses water, the cyclic compound, $\text{C}_{12}\text{H}_{17}\text{ON}_3$, melting at 150° and then at 205—207°, being produced. The *pyrazole* of camphor,

$\text{C}_8\text{H}_{14} \begin{array}{c} \text{C}:\text{CH} \\ \text{C}=\text{N} \end{array} \text{NH}$ or $\text{C}_8\text{H}_{14} \begin{array}{c} \text{C}-\text{CH} \\ \text{C}:\text{NH} \end{array} \text{N}$, melts at 149—150°.

Behaviour of the Hydroxymethylene Derivatives of Acyclic Ketones towards Semicarbazide.—The hydroxymethylene derivative of acetone alone reacts with semicarbazide to form a *disemicarbazone*, $\text{C}_6\text{H}_{11}\text{O}_2\text{N}_6$, which melts at 232°. When boiled with acids, it passes into *methylpyrazole*, $\text{C}_4\text{H}_6\text{N}_2$, which melts at 240°. The hydroxymethylene derivative of methyl ethyl ketone gives directly a cyclic compound, $\text{C}_6\text{H}_9\text{ON}_3$, which melts and decomposes at 164—165°. When boiled with dilute sulphuric acid, it yields 4:5-dimethylpyrazole, melting at 55—57°.

K. J. P. O.

Action of Carbon Disulphide on Hydrazo-compounds. PAUL JACOBSON and A. HUGERSHOFF [and, in part, EDW. JANKOWSKI and W. LISCHKE] (*Ber.*, 1903, 36, 3841—3857).—Hydrazo-compounds react more readily with carbon disulphide than azo-derivatives; with hydrazo-compounds, the reaction takes place readily at 150° and proceeds according to one or other of the two schemes (a) $\text{NHR} \cdot \text{NHR} + \text{CS}_2 = \text{NHR} \cdot \text{CS} \cdot \text{NHR} + \text{S}$, whereby a diarylated thiocarbamide and free sulphur are obtained; (b) with *p*-hydrazophenol ethers, $\text{C}_{14}\text{H}_{16}\text{ON}_2 + \text{CS}_2 = \text{C}_{15}\text{H}_{14}\text{ON}_2\text{S} + \text{H}_2\text{S}$, whereby cyclic compounds of the type of 2-thiol-6-ethoxy-1-phenylbenziminazole, $\text{SH} \cdot \text{C} \begin{array}{c} \text{NPh} \\ \text{N} \end{array} \text{C}_6\text{H}_3 \cdot \text{OEt}$, are produced.

A considerable amount of the hydrogen sulphide is used up in the reduction of the hydrazino-compounds to primary amines, which can then react with the carbon disulphide yielding open chain thiocarbamides. The yield of benziminazole compound is never more than 35 per cent. owing to these secondary reactions, and even when an excess of the azo-compound is introduced into the original mixture in order to react with the hydrogen sulphide and generate hydrazo-compounds, the yield is not improved.

s-Diphenylthiocarbamide, di-*p*-tolylthiocarbamide, di-*o*-tolylthiocarbamide, and phenyl-*o*-tolylthiocarbamide melting at 140°, have been obtained from the corresponding hydrazo-compounds.

2-Thiol-6-ethoxy-1-phenylbenziminazole (Jacobson and Fischer, *Abstr.*, 1892, 839), obtained from Bohn's benzenehydrazophenetole melting at 86° by the action of carbon disulphide at the ordinary temperature, or better at 150°, crystallises in long, felted needles, melts at 229°, is not hydrolysed by alkalis, and on treatment with mercuric oxide yields a compound, $\text{Hg}(\text{C}_{15}\text{H}_{13}\text{ON}_2\text{S})_2$, and with acetic anhydride and sodium acetate an *acetyl* derivative melting at 163—164°.

2-Thiol-6-ethoxy-1-*p*-tolylbenziminazole, obtained from Noeltling and

Werner's *p*-tolylhydrazophenetole (Abstr., 1891, 211), crystallises in colourless needles, melts at 205—206°, and yields an *acetyl* derivative melting at 145°. A secondary product is *p*-tolyl-*p*-phenetylthiocarbamide, melting at 134—135°.

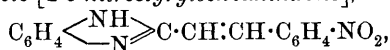
Benzenehydrazo-m-cresetole, $\text{NHPh}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OEt}$, forms colourless crystals melting at 100°, and with carbon disulphide at 150° yields 2-thiol-6-ethoxy-1-phenyl-4-methylbenziminazole, melting at 244—245° and sparingly soluble in alcohol. No *acetyl* derivative could be obtained.

Toluene-o-hydrazo-m-cresetole, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OEt}$, melting at 80°, yields 2-thiol-6-ethoxy-1-o-tolyl-4-methylbenziminazole, melting at 240°.

3:4-Dimethyl-4-ethoxyhydrazobenzene (compare Noelting and Werner, *loc. cit.*) yields with carbon disulphide 2-thiol-6-ethoxy-1-*p*-tolyl-5-methylbenziminazole, melting at 205—206° and identical with the compound obtained by the action of carbon disulphide on 2-amino-5-ethoxy-4:4'-dimethyldiphenylamine (Jacobson and Schwartz, Abstr., 1896, i, 26). A secondary product is di-*p*-tolylthiocarbamide.

Toluene-p-hydrazo-p-cresetole (Noelting and Werner, *loc. cit.*) melts at 55°, not at 153°, and with carbon disulphide at 160° yields *p*-tolyl-*p*-cresetylthiocarbamide, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OEt}$ [$\text{Me}_2\cdot\text{OEt} = 4:3':6'$], melting at 158°. J. J. S.

Chromophore Groupings. I. Methineammonium Dyes.
HANS RUPE and A. PORAI-KOSCHITZ (*Zeit. Farb. Text.-Chem.*, 1903, 2, 449—453. Compare Abstr., 1902, i, 40).—*o*-Nitrobenzylidene-2-methylbenziminazole [2-*o*-nitrostyrylbenziminazole],



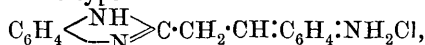
prepared by heating 2-methylbenziminazole with *o*-nitrobenzaldehyde for $\frac{3}{4}$ hour at 185—195°, crystallises from dilute alcohol in yellowish-green leaflets and melts at 215°; on reduction with stannous chloride and hydrochloric acid, it gives 2-*o*-aminostyrylbenziminazole, which crystallises from dilute alcohol in colourless needles, melts at 213°, and rapidly oxidises in the air; the *acetyl* derivative, $\text{C}_{17}\text{H}_{15}\text{ON}_3$, forms large needles and melts at 285°.

2-*m*-Nitrostyrylbenziminazole forms white needles decomposing at 220° and is unstable; the *hydrochloride* forms white needles. 2-*m*-Aminostyrylbenziminazole, $\text{C}_{15}\text{H}_{13}\text{N}_3\cdot\frac{1}{2}\text{H}_2\text{O}$, crystallises from dilute alcohol or acetic acid in white needles and melts at 116° losing its water of crystallisation, the anhydrous substance subsequently melting at 153°; the *hydrochloride*, $\text{C}_{15}\text{H}_{13}\text{N}_3\cdot 2\text{HCl}$, crystallises in stellate aggregates of needles, and the *platinichloride*, $\text{C}_{15}\text{H}_{13}\text{N}_3\cdot\text{H}_2\text{PtCl}_6$, forms white needles.

2-*p*-Nitrostyrylbenziminazole crystallises from alcohol and melts and decomposes at 269—270°; it is extraordinarily sensitive to oxidation and could not be obtained pure; the *hydrochloride* crystallises from dilute alcohol in white needles. 2-*p*-Aminostyrylbenziminazole, $\text{C}_{15}\text{H}_{13}\text{N}_3\cdot\text{H}_2\text{O}$, melts at 225° and cannot be recrystallised; the *hydrochloride*, $\text{C}_{15}\text{H}_{13}\text{N}_3\cdot 2\text{HCl}$, forms orange-red, and the *sulphate*

$C_{15}H_{13}N_3H_2SO_4$, yellow needles; the *acetyl* derivative, $C_{17}H_{15}ON_3$, has a high melting point.

The azo-compounds derived from 2-*p*-aminostyrylbenziminazole dye cotton directly faster shades than the azo-compounds derived from the corresponding *m*-amino-compound, whilst these are faster than the *o*-amino-dyes. It is noteworthy that the para- and ortho-aminostyrylbenziminazoles can, in the form of their salts with mineral salts, dye silk and wool, whilst the meta-bases entirely lack this property. It is suggested that the ortho- and para-compounds owe their tinctorial power to the possibility of their forming coloured quinonoid salts of the type



whilst the meta-derivative,



is colourless.

W. A. D.

Researches on Azo-compounds. New Mode of Formation of Indazole Derivatives. PAUL FREUNDLER (*Compt. rend.*, 1903, 137, 982—984. Compare Abstr., 1903, i, 584).—*o*-Hydrazobenzoic acetal decomposes in neutral solution into methyl alcohol and

o-indazylbenzylacetal, $C_6H_4 \begin{array}{c} \text{N} \\ | \quad | \\ \text{CH} \end{array} > N \cdot C_6H_4 \cdot CH(OMe)_2$, which, on further warming, is partially transformed into *o*-indazylbenzaldehyde, $C_6H_4 \begin{array}{c} \text{N} \\ | \quad | \\ \text{CH} \end{array} > N \cdot C_6H_4 \cdot CHO$, which crystallises from ether

in long, white needles and melts at 94.5—95°. It dissolves in boiling nitric acid without oxidation; on cooling, the *nitrate* crystallises in needles decomposed by water. The *hydrazone* crystallises in small, yellow prisms melting and decomposing at 191°.

o-Azobenzaldehyde is almost instantly decolorised by warming with 10 per cent. sulphuric acid, forming *o*-indazylbenzoic acid, together with a small quantity of a substance not yet identified.

C. H. D.

3:5-Dibromo-2-aminobenzoic Acid and its Nitrile. Synthesis of Quinazolines. MARSTON T. BOGERT and WILLIAM F. HAND (*J. Amer. Chem. Soc.*, 1903, 25, 935—947).—*o*-Aminobenzonitrile (Bogert and Hand, Abstr., 1903, i, 292) is converted into 3:5-dibromo-2-aminobenzonitrile by bromination with a solution of bromine in carbon tetrachloride, benzene, or water, by alkaline potassium hypobromite, or, preferably with an acidified solution of potassium bromide and bromate. It separates from alcohol in small, white, feathery needles and melts at 156—156.5° (corr.). It does not form a salt when hydrogen chloride is passed into its ethereal solution, neither does it form an acetyl compound when boiled with acetic anhydride. When hydrolysed, it forms 3:5-dibromo-2-aminobenzoic acid, crystallising from alcohol in white needles and melting at

235.6—236° (corr.). This acid can be conveniently prepared by brominating anthranilic acid with a mixture of potassium bromide and bromate in presence of hydrochloric acid. When heated at 260—270°, it decomposes with evolution of hydrogen bromide. Its *barium* salt is sparingly soluble in cold water and crystallises with 2H₂O. By elimination of the amino-group from 3:5-dibromo-2-aminobenzoic acid, 3:5-dibromobenzoic acid is formed, the barium salt of which crystallises with 3½H₂O.

The elimination of the amino-group from 3:5-dibromo-2-aminobenzonitrile takes place with great difficulty, and the yield of 3:5-dibromobenzoic acid is very small.

When 3:5-dibromo-2-aminobenzonitrile is heated with formic acid at 225—235°, it forms 6:8-dibromo-4-ketodihydroquinazoline, $\text{CH}\cdot\text{CBr}\cdot\text{C}\text{---}\text{N}\text{:CH}$
 $\text{CBr}\cdot\text{CH}\cdot\text{C}\cdot\text{CO}\cdot\text{NH}$ (compare Bogert and Hand, *loc. cit.*; Bogert, Breneman, and Hand, *Abstr.*, 1903, i, 527). It crystallises in small needles and decomposes above 300°. Its *ethyl ether* separates from alcohol in snow-white needles and melts at 229—230° (corr.).

6:8-Dibromo-2-methyl-4-ketodihydroquinazoline, prepared by heating the nitrile with acetic anhydride at 220—230°, separates from aniline in snow-white crystals which begin to decompose at 300°. Its *ethyl ether* begins to decompose at about 170°.

6:8-Dibromo-2-ethyl-4-ketodihydroquinazoline, prepared from the nitrile and propionic anhydride, crystallises from dilute alcohol in silky needles and melts at 278—280° (corr.).

6:8-Dibromo-2-n-propyl-4-ketodihydroquinazoline crystallises from dilute alcohol in colourless, microscopic needles and melts at 238—240° (corr.).

6:8-Dibromo-2-isopropyl-4-ketodihydroquinazoline melts at 259—260° (corr.).

6:8-Dibromo-2-isobutyl-4-ketodihydroquinazoline forms colourless, microscopic needles and melts at 230—231.5° (corr.).

6:8-Dibromo-2-methyl-4-thioketodihydroquinazoline, prepared by heating 3:5-dibromo-2-aminobenzonitrile with thioacetic acid at 220—230°, crystallises from aniline in yellow needles and does not melt at 290°. Its *ethyl ether* forms light yellow needles and begins to decompose at about 305°.

A. McK.

Indanthrene and Flavanthrene. I. ROLAND SCHOLL (*Ber.*, 1903, 36, 3410—2426, 3710. Compare Hinsberg, *Abstr.*, 1902, i, 238).—Indanthrene A, *N*-dihydro-1:2:2':1'-anthraquinonazine (following abstract), differs from most of the other derivatives of dihydrophenazine in its remarkable stability, and shows very little tendency to undergo oxidation.

Its constitution follows from its method of formation, the para-position of the NH groups being deduced from the fact that it does not yield a diamine on reduction.

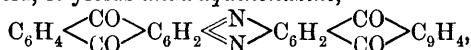
The paper contains a discussion on the constitution of indanthrene, and of the relationship between the constitution and the stability and colour of the compound.

J. J. S.

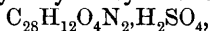
Indanthrene and Flavanthrene. II. ROLAND SCHOLL and HANS BERBLINGER (*Ber.*, 1903, **36**, 3427—3445. Compare Abstr., 1903, i, 446, 530, 582).—Indanthrene A, *N*-*dihydro*-1 : 2 : 1' : 2'-*anthraquinonazine*, $C_6H_4 \begin{smallmatrix} \diagup CO \diagdown \\ \diagdown CO \diagup \end{smallmatrix} C_6H_2 \begin{smallmatrix} \diagup NH \diagdown \\ \diagdown NH \diagup \end{smallmatrix} C_6H_2 \begin{smallmatrix} \diagup CO \diagdown \\ \diagdown CO \diagup \end{smallmatrix} C_6H_4$ (Abstr., 1902, i, 721), is obtained when β -aminoanthraquinone is fused at 250° for half an hour with 5 times its weight of potassium hydroxide and 1/5th of its weight of potassium nitrate. The product is boiled with water and the insoluble dye removed and reduced by treatment with sodium hydroxide and sodium hyposulphite at 60—70°. The sodium derivative is thus obtained in the form of well-developed needles with a coppery lustre, and when dissolved in water and oxidised by atmospheric oxygen is reconverted into indanthrene A. By this process, indanthrene B, which is also present, is removed.

Indanthrene A is practically insoluble in the usual organic solvents and is only very sparingly soluble in boiling aniline or nitrobenzene. It dissolves in hot quinoline (1 : 500), and the blue solution deposits blue needles with a coppery lustre somewhat resembling indigotin. When gently heated, it partly sublimes and is completely decomposed at 470—500°. It is only feebly basic, and its salts are readily decomposed by water.

When oxidised in concentrated sulphuric acid solution with nitric or chromic acid, it yields *anthraquinonazine*,

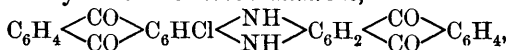


which, on crystallisation from hexachlorobenzene or from nitrobenzene, forms greenish-yellow, flat prisms or hexagonal plates. Its salts with strong acids are slowly hydrolysed by water. The *sulphate*,



forms spindle-shaped rhombohedra. The base is readily reconverted into indanthrene even by simply heating with solvents of high boiling point containing hydrogen, for example, quinoline, phenol, or even nitrobenzene. When transferred to cotton fabrics, it is slowly reduced, probably at the expense of the cellulose. Indanthrene combines with anthraquinonazine to yield a compound of the type of quinhydrone. This is termed *anthraquinonazhydrine*, $C_{56}H_{26}O_8N_4$, and is formed as an intermediate product in the oxidation of indanthrene or in the reduction of anthraquinonazine. It crystallises in green, flat prisms, possesses only feebly basic properties, and is readily transformed, even during recrystallisation, into indanthrene.

A theoretical yield of 4-*chloroindanthrene*,

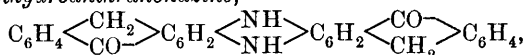


is obtained when anthraquinonazine is boiled for 1 hour with concentrated hydrochloric acid. It crystallises from quinoline in deep blue needles. The technical product, indanthrene C (D.R.-P. 138167), obtained by the action of bromine at 60—80° on indanthrene dissolved in concentrated sulphuric acid, is a mixture of *di*- and *tri*-*bromoindanthrenes* which may be separated by crystallisation from quinoline.

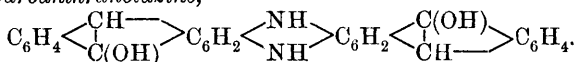
4-*Aminoindanthrene*, obtained by the action of concentrated aqueous ammonia on anthraquinonazine at 200°, is a somewhat dirty blue

product. The corresponding *anilino*-compound has a deep purple blue colour.

Indanthrene, on reduction with hydriodic acid and red phosphorus, yields *N-dihydroanthranonazine*,

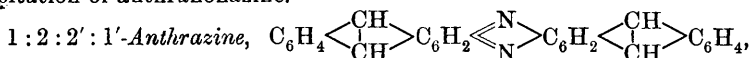


in the form of a yellowish-brown powder; it is only sparingly soluble in the usual organic solvents, but dissolves in concentrated acids. It also dissolves in alcoholic solutions of alkalis yielding soluble salts of *N-dihydroanthranolazine*,



Solutions of these alkali salts, when diluted with water, exhibit a greenish-yellow fluorescence. Between 334° and 344° (corr.), it decomposes into hydrogen and anthranonazine, and a similar but slower change occurs when it is boiled with nitrobenzene.

Anthranonazine, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} \text{C}_6\text{H}_2 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{C}_6\text{H}_2 \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{C}_6\text{H}_4$, crystallises from nitrobenzene in brownish-red, prismatic needles with a green, metallic lustre. It begins to sublime at 360° , giving off a violet-red vapour. Its solutions are magenta-red in colour and exhibit no fluorescence. In the indanthrene, as in the anthracene series (Liebermann, Abstr., 1880, 665), fluorescence is only met with in those compounds having a *para*-linking joining the *meso*-carbon atoms. It dissolves in alcoholic alkalis yielding characteristic blue solutions of the metallic derivatives of anthranolazine. The addition of water to the blue solutions causes an immediate change of colour to red and the precipitation of anthranonazine.

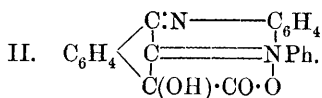
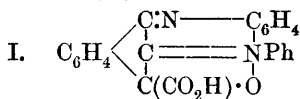


obtained by distilling indanthrene with zinc dust under reduced pressure, or by reducing the dye with hydriodic acid and red phosphorus at $210\text{--}220^\circ$, crystallises from nitrobenzene in brownish-yellow, prismatic needles. In dilute solutions, it exhibits a greenish-yellow fluorescence. It sublimates at about 340° and melts at about 390° (corr.), and is soluble in concentrated sulphuric or nitric acids. J. J. S.

Oxidation of Rosindone and Naphthaphenazine by Chromic Acid. OTTO FISCHER (*Ber.*, 1903, 36, 3622—3626).—The rosindonic acid, obtained by the oxidation of rosindone by chromic acid (Fischer and Hepp, Abstr., 1891, 1044), is shown not to be the primary product but to be produced by the transformation of the isomeric *isorosindonic* acid.

When rosindone is oxidised by chromic acid and acetic acid, the temperature of the reaction not being allowed to exceed $70\text{--}80^\circ$, very little rosindonic acid is formed; the main product, *isorosindonic acid*, dissolves in concentrated sulphuric acid to give a violet-red coloration, whilst rosindonic acid gives a deep yellow coloration. The *iso*-acid separates from a mixture of methylal and light petroleum in white prisms, which soften at 180° and melt at about 206° with evolution of

carbon dioxide. In contact with 10—15 parts of concentrated sulphuric acid, it undergoes transformation into the isomeric rosindonic acid in 10—15 minutes at the ordinary temperature, or in a few seconds if the mixture be gently warmed. Rosindonic acid crystallises from ethyl acetoacetate in plates and melts at 227—228°. The following formulæ probably represent rosindonic acid (I) and isorosindonic acid (II) :



When $\alpha\beta$ -naphthaphenazine is oxidised by chromic acid, it forms $\alpha\beta$ -diketonaphthaphenazine, which separates from a mixture of chloroform and light petroleum in needles and melts and decomposes at 265° (compare Lindenbaum, Abstr., 1901, i, 423). When the green solution obtained by dissolving $\alpha\beta$ -diketonaphthaphenazine in sodium hydroxide is acidified with hydrochloric acid, *indenophenazineglycollic acid*, $\text{C}_6\text{H}_4 \begin{array}{c} \text{N:C} \cdot \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{N:C} \cdot \text{C}(\text{OH}) \cdot \text{CO}_2\text{H} \end{array}$, is formed; this melts at 223—224°, and, like rosindonic acid, forms a yellow solution with concentrated sulphuric acid.

A. McK.

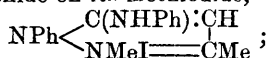
Anilopyrine and 5-Anilino-1-phenyl-3-methylpyrazole. AUGUST MICHAELIS and E. HEPNER (*Ber.*, 1903, 36, 3271—3279. Compare Stolz, following abstract).—The substance considered by Michaelis and Gunkel (Abstr., 1901, i, 351) to be anilopyrine is in reality 5-anilino-

1-phenyl-3-methylpyrazole, $\text{NPh} \begin{array}{c} \text{C}(\text{NHPH}) \cdot \text{CH} \\ \diagup \quad \diagdown \\ \text{N} \text{====} \text{CMe} \end{array}$; this is shown by the fact that it is obtained by heating propylantipyryne chloride, $\text{NPh} \begin{array}{c} \text{CCl} \text{====} \text{CH} \\ \diagup \quad \diagdown \\ \text{NPrCl} \cdot \text{CMe} \end{array}$, with aniline at 200°, just as it is formed from antipyryne chloride (5-chloro-1-phenyl-3-methylpyrazole 2-methochloride) under similar conditions. The true *anilopyrine*,

$\text{NPh} \begin{array}{c} \text{C} \text{====} \text{CH} \\ \diagup \quad \diagdown \\ \text{NPh} \quad \text{NMe} \end{array}$, however, is obtained by heating antipyryne

chloride with aniline (2 mols.) for 2 hours at 125° and decomposing the product with sodium hydroxide; in these circumstances, the compound,

$\text{NPh} \begin{array}{c} \text{C}(\text{NHPH}) \cdot \text{CH} \\ \diagup \quad \diagdown \\ \text{NMeCl} \text{====} \text{CMe} \end{array}$, initially formed, loses hydrogen chloride, and not methyl chloride as is the case at 200°. Anilopyrine can also be obtained from 5-anilino-1-phenyl-3-methylpyrazole by the action of sodium hydroxide on its methiodide,

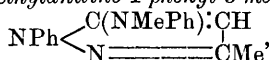


it melts at 58—59°, is strongly basic, and reduces warm solutions of silver salts. The *hydrochloride* is a white, crystalline, deliquescent substance. The *platinichloride*, $(\text{C}_{17}\text{H}_{17}\text{N}_3)_2 \cdot \text{H}_2\text{PtCl}_6$, forms thick, reddish-yellow crystals, melts at 203°, and is identical with the

platinichloride of 5-anilino-1-phenyl-3-methylpyrazole methochloride, $\text{NPh} \begin{smallmatrix} \text{C}(\text{NHPH})\cdot\text{CH} \\ \text{NMeCl} = \text{CMe} \end{smallmatrix}$; the analogous *aurichloride* crystallises in slender, reddish-yellow needles and melts at 125° . The *hydriodide* is identical with 5-anilino-1-phenyl-3-methylpyrazole 2-methiodide and forms thick, white, lustrous crystals melting at 174° ; the *picrate*, $\text{C}_{23}\text{H}_{20}\text{O}_6\text{N}_6$, melts at 170° , and the *dichromate*, $(\text{C}_{17}\text{H}_{17}\text{N}_3)_2\text{H}_2\text{Cr}_2\text{O}_7$, at 185° .

Anilopyrine methiodide, $\text{NPh} \begin{smallmatrix} \text{C}(\text{NMePh})\cdot\text{CH} \\ \text{NMeI} = \text{CMe} \end{smallmatrix}$, formed with explosive violence by the union of the components, crystallises in rhombic plates and melts at 194° ; the analogous *ethiodide*, $\text{C}_{19}\text{H}_{22}\text{N}_3\text{I}$, melts at $184\text{--}185^\circ$ and the *propiodide* at 134° .

ψ -*Anilopyrine* (5-methylanilino-1-phenyl-3-methylpyrazole),



is obtained by heating anilopyrine methiodide, when methyl iodide distils off, or by digesting antipyrine chloride with methylaniline at 200° ; it crystallises from alcohol in slender, transparent crystals, melts at 88.5° , and boils at $220\text{--}228^\circ$ under 20 mm. pressure. The *platinichloride*, $(\text{C}_{17}\text{H}_{17}\text{N}_3)_2\text{H}_2\text{PtCl}_6$, forms slender, yellow needles and melts and decomposes at $208\text{--}212^\circ$; the methiodide is identical with the methiodide of anilopyrine.

W. A. D.

5-Imino-1-phenyl-2:3-dimethylpyrine. FRIEDRICH STOLZ (*Ber.*, 1903, 36, 3279—3290).—The substance described by Michaelis and Gunkel (*Abstr.*, 1901, i, 351) as iminopyrine is identical with Walther's 5-amino-1-phenyl-3-methylpyrazole (*Abstr.*, 1897, i, 297). The true *iminopyrine* (5-imino-1-phenyl-2:3-dimethylpyrazolone), for which the author prefers the formula $\text{NPh} \begin{smallmatrix} \text{C}(\text{:NH})\cdot\text{CH} \\ \text{NMe} - \text{CMe} \end{smallmatrix}$ analogous to Knorr's structure for antipyrine (compare Michaelis and Hepner, preceding abstract), is obtained by heating antipyrine chloride (5-chloro-1-phenyl-3-methylpyrazole 2-methochloride) with aqueous ammonia for 6 hours at $125\text{--}150^\circ$ or with ammonium carbonate for 12 hours at 200° ; it forms hygroscopic crystals, melts at 63° , is strongly basic, and rapidly absorbs carbon dioxide from the air, forming the *carbonate*, $\text{C}_{11}\text{H}_{13}\text{N}_3\cdot\text{H}_2\text{CO}_3\cdot\text{H}_2\text{O}$, which crystallises from alcohol in colourless prisms. *Iminopyrine hydrochloride*, $\text{C}_{11}\text{H}_{13}\text{N}_3\cdot\text{HCl}$, separates from absolute alcohol in well-formed crystals and melts at 192° ; the *platinichloride* melts at 207° , the *hydrobromide* at 196° , and the *picrate* at 191° . *Iminopyrine-ethylurethane*, $\text{C}_{11}\text{H}_{12}\text{N}_3\cdot\text{CO}_2\text{Et}$, prepared by shaking the carbonate with a solution of sodium hydroxide and ethyl chlorocarbonate, crystallises from alcohol in large prisms and melts at 178° .

Benzoyliminopyrine, $\text{C}_{18}\text{H}_{17}\text{ON}_3$, prepared by benzoylating iminopyrine, crystallises from dilute alcohol in striated prisms and melts at 176° . *Benzenesulphonyliminopyrine*, $\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2\text{S}$, obtained by the interaction of the base with benzenesulphonic chloride, crystallises in prisms and melts at 211° .

5-Methylimino-1-phenyl-2:3-dimethylpyrazolone, obtained by heating iminopyrine with methyl iodide and methyl alcohol at 100—125°, or, preferably, by the interaction of methylamine and 5-chloro-1-phenyl-3-methylpyrazole 2-methochloride during 8 hours at 150°, gives a *picrate* which crystallises in lustrous, golden needles and melts at 131°; the *methiodide*, $C_{13}H_{18}N_3I$, crystallises from alcohol, on adding ether, in colourless needles, melts at 183°, and can also be obtained by heating iminopyrine carbonate with an excess of methyl iodide and methyl alcohol for 12 hours at 125°.

5-Ethylimino-1-phenyl-2:3-dimethylpyrazolone, prepared by heating antipyrine chloride with ethylamine at 125°, gives a *picrate* melting at 110°.

5-Imino-1-phenyl-2:3:4-trimethylpyrazolone, obtained by heating 5-chloro-1-phenyl-3:4-dimethylpyrazole-2-methochloride (Michaelis, Voss and Greiss, Abstr., 1901, i, 407) with aqueous ammonia for 6 hours at 100—150°, gives a *carbonate* which separates from alcohol in large crystals, a *picrate* which melts at 115°, and an acid *chromate*, $2C_{12}H_{15}N_3 \cdot 3CrO_3$, melting at 115—116°. The *benzoyl* derivative, $C_{19}H_{19}ON_3 \cdot H_2O$, crystallises from water in lustrous prisms and melts at 146°.

5-Methylimino-1-phenyl-2:3:4-trimethylpyrazolone closely resembles the preceding compound; the *picrate* melts at 123° and the *methiodide* at 130°.

3-Imino-1-phenyl-2:5-dimethylpyrazolone, $NPh \begin{smallmatrix} \text{CMe} \cdot \text{CH} \\ \text{NMe} \cdot \text{C} \cdot \text{NH} \end{smallmatrix}$, prepared from 3-chloro-1-phenyl-5-methylpyrazole 2-methochloride (*iso*-antipyrine chloride) and aqueous ammonia at 150°, gives a crystalline *carbonate* and *picrate*.
W. A. D.

o-Dianisylthiodicyanodiamine. H. KLUT (Ber., 1903, 36, 3322—3325).—*o*-Dianisylthiodicyanodiamine,

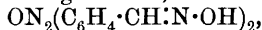
$OMe \cdot C_6H_4 \cdot NH \cdot C(NH) \cdot NH \cdot CS \cdot NH \cdot C_6H_4 \cdot OMe$, prepared by the action of sulphur dichloride or thiophosgene on a chloroform solution of *o*-anisylthiocarbamide (compare the formation of thiodicyanodiamine from thiocarbamide, Rathke, Abstr., 1879, 41), separates from a mixture of benzene and light petroleum in white leaflets, melting at 80—82°, is a monacidic base, insoluble in water but easily soluble in most organic solvents, and becomes dark yellow on exposure to light. Its *picrate* softens at 175° and melts completely at 198°. Its *monoacetyl* derivative crystallises from alcohol in rhombic leaflets and melts at 205—206°. Its *nitrite* melts at 129°, and, when warmed with water, forms the *nitroso*-derivative,

$OMe \cdot C_6H_4 \cdot N(NO) \cdot C(NH) \cdot NH \cdot CS \cdot NH \cdot C_6H_4 \cdot OMe$, which separates from alcohol in orange-coloured, prismatic needles and melts at 171—172°.

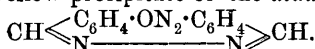
o-Dianisylthiodicyanodiamine unites with phenylcarbimide to form the compound, $C_{16}H_{18}O_2N_4S \cdot PhN : CO$, which crystallises from dilute alcohol in tiny leaflets and melts at 185°. The corresponding compound with phenylthiocarbimide melts at 210—211°.

A. McK.

***m*-Azoxybenzaldehyde and its Analogues.** ALFRED HUMAN and HUGO WEIL (*Ber.*, 1903, 36, 3469—3475).—*m*-Azoxybenzaldehyde has been prepared by Alway (Abstr., 1903, i, 201, 706). A 70 per cent. yield is obtained by the reduction of *m*-nitrobenzaldehyde with ferrous hydroxide. On extracting the product with a solution of sodium hydrogen sulphite and boiling with sulphuric acid, the azoxy-compound is precipitated. In its condensations, both aldehyde groups react simultaneously. The *bisphenylhydrazones*, $\text{ON}_2(\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{NHPH})_2$, forms yellow crystals melting at 198° , the *dioxime*,

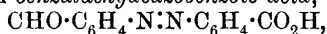


melts at 191° . When boiled with it, aniline reacts slowly, yielding *m*-azoxybenzylideneaniline, which forms yellow crystals melting at 125° . Hydrazine forms a yellow precipitate of the *aldazine*,



Dimethylaniline and sulphuric acid form *m*-azoxyleucomalachite-green, $\text{ON}_2[\text{C}_6\text{H}_4\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2]_2$, melting at 176° and yielding a yellowish-green dye on oxidation with lead peroxide.

Heating with concentrated sulphuric acid at 110° converts *m*-azoxybenzaldehyde into *m*-benzaldehydeazobenzoic acid,



melting at 163° . The *sodium* salt is partially hydrolysed by water. The *ethyl* ester melts at 156° . Hydrazine forms the *aldazine*, melting above 330° . The *oxime* forms yellow crystals which melt at 185° . The compound with phenylhydrazinesulphonic acid was also prepared. *Benzylideneanilineazobenzoic acid*, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{NPh}$, is faintly yellow coloured and melts at 128° .

p-Azoxybenzaldehyde (compare Alway, Abstr., 1902, i, 649) may be prepared in similar manner. Concentrated sulphuric acid converts it into *p*-benzaldehydeazobenzoic acid, melting above 330° and forming an *ethyl* ester melting at 60° . C. H. D.

***m*-Azoxybenzaldehyde and its Analogues.** ALFRED HUMAN and HUGO WEIL (*Ber.*, 1903, 36, 3801—3802. Compare preceding abstract).—To ascertain whether the intermolecular rearrangement of *m*-azoxybenzaldehyde into benzaldehydazobenzoic acid, which takes place when it is acted on by concentrated sulphuric acid, is not due to the oxidising influence of one molecule of the azo-compound on a second, the reaction was carried out in presence of the easily oxidisable benzaldehyde; this was, however, recovered unchanged. The rearrangement is thus apparently a consequence of the oxidation of the aldehyde group of the distant nucleus, by the oxygen atom attached to nitrogen. E. F. A.

The Three Isomeric Nitronitrosobenzenes. EUGEN BAMBERGER and RUDOLF HÜBNER (*Ber.*, 1903, 36, 3803—3822).—Alway (Abstr., 1903, i, 690) has prepared *m*-nitronitrosobenzene by oxidising the solution obtained from the reduction of *m*-dinitrobenzene with zinc and acetic acid. The authors had examined this action before the publication of Alway's paper, and the results have been partly published (Hübner, *Inaug. Diss.*, Zürich, 1902).

o-Nitronitrosobenzene, $\text{ON}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, prepared by oxidising *o*-nitroaniline with Caro's acid, separates from water in almost colourless needles and melts at $126\text{--}126.5^\circ$ to a green liquid. Small amounts of *o*-dinitrobenzene and *o*-*o'*-dinitroazoxybenzene were also isolated from the product of the oxidation.

m-Nitronitrosobenzene, prepared from *m*-nitroaniline and Caro's acid, separates from water in colourless, glistening needles and melts at $89.5\text{--}90.5^\circ$ to a green liquid (Alway gives 85°). *m*-*m'*-Dinitroazoxybenzene, produced during the oxidation in about the same amount as *m*-nitronitrosobenzene, separates from concentrated nitric acid in yellow needles and melts at $144\text{--}145^\circ$. A trace of *m*-dinitrobenzene was also formed during the oxidation.

p-Nitronitrosobenzene, prepared from *p*-nitroaniline and Caro's acid, separates from alcohol in orange-coloured needles and melts at $118.5\text{--}119^\circ$ to a green liquid. When oxidised, it readily yields *p*-dinitrobenzene.

p-*p'*-Dinitroazoxybenzene, melting at 222° , is also formed during the oxidation.

p-Nitroazobenzene, prepared by adding aniline to a solution of *p*-nitronitrosobenzene in glacial acetic acid, forms salmon-coloured leaflets or flat needles and melts at $134\text{--}135^\circ$. *m*-Nitroazobenzene was prepared in an analogous manner, and also by combination of nitrosobenzene and *m*-nitroaniline.

o-*o'*-Dinitroazoxybenzene, prepared by the action of alcoholic potash on *o*-nitronitrosobenzene, crystallises in flat, glistening needles and melts at $175\text{--}175.5^\circ$. The filtrate, from which the crude *o*-*o'*-dinitroazoxybenzene had been removed, was extracted with ether and then acidified; nitrous acid was formed, and *o*-nitro-*o'*-hydroxyazoxybenzene, crystallising in silky needles and melting at $91\text{--}92^\circ$, was precipitated. Evidence for its constitution was further adduced by its behaviour on reduction, when *o*-aminophenol and *o*-phenylenediamine were formed.

o-Nitronitrosobenzene, when boiled with water, gives *o*-nitro-*o'*-hydroxyazoxybenzene, *o*-*o'*-dinitroazoxybenzene, *o*-dinitrobenzene, *o*-nitrophenol, *o*-nitroaniline, and other products contained in a tar, which was not further examined.

o-Dinitrobenzene is easily prepared by oxidising *o*-nitronitrosobenzene.

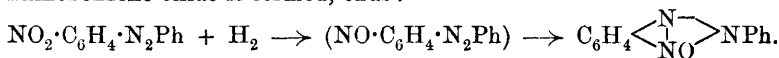
A series of *o*-nitroazo-derivatives, prepared by the condensation of *o*-nitronitrosoaryl derivatives with aromatic amines, is described. *o*-Nitroazobenzene, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Ph}$, prepared from *o*-nitronitrosobenzene and aniline, separates from alcohol in glassy, orange-coloured prisms and melts at $70.5\text{--}71^\circ$. *o*-Nitrobenzene-*o*-azotoluene, prepared from *o*-nitronitrosobenzene and *o*-toluidine, separates from alcohol in orange-coloured needles and melts at 85° . *o*-Nitrobenzene-*p*-azotoluene separates from alcohol in silky, orange-red needles and melts at 88° . *o*-Nitrobenzeneazo-*p*-chlorobenzene, prepared from *o*-nitronitrosobenzene and *p*-chloroaniline, crystallises in orange-red leaflets with greenish-golden lustre and melts at $145\text{--}146^\circ$. *o*-Nitrobenzeneazo-2 : 4-dichlorobenzene, prepared from *o*-nitronitrosobenzene and 2 : 4-dichloroaniline, separates

from alcohol in salmon-coloured, silky needles and melts at 155.5° . *o*-Nitrobenzeneazo-2 : 4 : 6-trichlorobenzene, prepared from *o*-nitronitrosobenzene and 2 : 4 : 6-trichloroaniline, separates from alcohol in straw-coloured, glistening leaflets and melts at 143° . *o*-Nitrobenzeneazo-*p*-bromobenzene, prepared from *o*-nitronitrosobenzene and *p*-bromoaniline, forms brick-red leaflets of greenish-golden lustre and melts at 152.5° .

4-Nitroso-3-nitrotoluene, prepared by oxidising *m*-nitro-*p*-toluidine by Caro's acid, separates from alcohol in greenish-yellow needles and melts at $145-145.5^{\circ}$. By combination with aniline, it forms 2-nitro-*p*-tolueneazobenzene, which crystallises in glistening leaflets or needles and melts at $71-71.5^{\circ}$ A. McK.

Reduction of *o*-Nitroazo-compounds. EUGEN BAMBERGER and RUDOLF HÜBNER (*Ber.*, 1903, 36, 3822—3827. Compare preceding abstract).—Whilst nitroso-compounds, on account of the ease with which they are reduced, can be detected only with some difficulty during the reduction of nitro-compounds, the case is otherwise with *o*-nitroazo-compounds. The nitroso-derivative, presumably the initial product of the reduction of *o*-nitroazo-compounds, is not further reduced, but undergoes intramolecular rearrangement into the stable "azoimino-oxides."

When *o*-nitroazobenzene is reduced by sodium sulphide, benzeneazoiminobenzene oxide is formed, thus :



The latter substance separates from light petroleum in glistening needles and melts at 88.5° . It is reduced by tin and hydrochloric acid to phenylazoiminobenzene, $\text{C}_6\text{H}_4 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{NPh}$, melting at 109.5° and identical with the compound described by Gattermann and Wichmann (*Abstr.*, 1888, 829) as 2-phenylphenotriazole.

p-Bromophenylazoiminobenzene oxide, $\text{C}_6\text{H}_4 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \quad \text{O} \end{array} \text{N} \cdot \text{C}_6\text{H}_4\text{Br}$, prepared by the reduction of *o*-nitrophenylazo-*p*-bromobenzene by sodium sulphide, forms white, glistening needles and melts at $162-162.5^{\circ}$. When reduced by stannous chloride and concentrated hydrochloric acid, it forms *p*-bromophenylazoiminobenzene, $\text{C}_6\text{H}_4 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{N} \cdot \text{C}_6\text{H}_4\text{Br}$, which separates from alcohol in silky needles and melts at 174° .

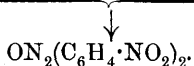
p-Chlorophenylazoiminobenzene oxide crystallises in needles and melts at $155.5-156.5^{\circ}$. On reduction by stannous chloride, it yields *p*-chlorophenylazoiminobenzene, which crystallises in needles and melts at $167.5-168.5^{\circ}$.

Phenylazoiminotoluene oxide, $\text{C}_6\text{H}_3\text{Me} \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \quad \text{O} \end{array} \text{NPh}$, prepared from 2-nitro-*p*-tolueneazobenzene and sodium sulphide, crystallises in slightly yellow leaflets and melts at 142.5° . When reduced by

stannous chloride, it forms *phenylazoiminotoluene*, which separates from alcohol in glistening prisms and melts at 98.5° .

A. McK.

Oxidation of *p*-Phenylenediamine. EUGEN BAMBERGER and RUDOLF HÜBNER (*Ber.*, 1903, 36, 3827—3831. Compare preceding abstracts).—*p*-Nitroaniline is the main product of the oxidation of *p*-phenylenediamine in aqueous solution by Caro's acid. This is an instance of the ease with which the hydroxylamino-group is oxidised as compared with the amino-group, since the reaction undoubtedly proceeds thus: $\text{C}_6\text{H}_4(\text{NH}_2)_2 \rightarrow (\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{OH} \rightarrow \text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}) \rightarrow \text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$. A comparatively small part of the *p*-nitroaniline, formed in this manner, is further oxidised with the production of *p*-dinitrobenzene and *p-p'*-dinitroazoxybenzene, thus: $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \rightarrow (\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{OH} \rightarrow \text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}) \rightarrow \text{C}_6\text{H}_4(\text{NO}_2)_2$



When the oxidation of *p*-phenylenediamine by Caro's acid is conducted in ethereal solution, *p*-nitrosoaniline can be isolated as well as *p*-nitroaniline.

A. McK.

Liquid Crystals. RUDOLF SCHENCK and ERNST EICHWALD (*Ber.*, 1903, 36, 3873—3877. Compare Abstr., 1898, ii, 286, 593; 1899, ii, 360; 1900, ii, 339; Rotarski, Abstr., 1903, i, 869; ii, 137).—*p*-Azoxyanisole, even after several crystallisations from methyl alcohol, contains small amounts (1.5 per cent.) of *p*-azoanisole. The presence of this impurity is readily detected by the red colour which it develops on the addition of hydrochloric acid, and it may be completely removed by crystallising the azoxyanisole several times from a mixture of concentrated hydrochloric acid (1 part) and glacial acetic acid (3 parts). The pure product forms pale yellow prisms, melts to a cloudy liquid at 116° , and suddenly becomes clear at 135.2° . Rotarski's statement that, when free from *p*-azoanisole, the azoxy-compound melts immediately to a clear liquid is not correct.

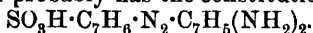
When *p*-azoxyanisole is kept for some time at 130° , small amounts of *p*-azoanisole are formed.

J. J. S.

A New Sensitive Indicator from *m*-Toluidine. JULIUS TRÖGER and W. HILLE (*J. pr. Chem.*, 1903, [ii], 68, 297—309).—The action of sulphur dioxide on diazotised *m*-toluidine in very dilute sulphuric acid solution leads to the formation of a *sulphonic acid*, $\text{C}_{14}\text{H}_{15}\text{N}_4\text{SO}_3\text{H}$, as a blood-red, voluminous precipitate. On adding its potassium salt to dilute hydrochloric acid, the sulphonic acid is obtained in ruby-red, prismatic needles. It decomposes at 100° , evolves sulphur dioxide when heated, is only slightly soluble in water, forming a carmine solution, and dissolves in aqueous alkali hydroxides or carbonates, or ammonia to form yellow solutions from which it is liberated by mineral acids, but not by acetic acid. As an indicator, the sulphonic acid is used in the form of its sodium salt; in its colorations and scope of application, it resembles, but is more sensitive than, helianthin.

The *potassium*, *sodium*, *barium*, and *ammonium* salts are described.

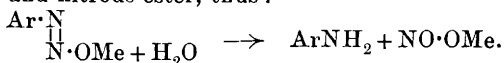
The sulphonic acid probably has the constitution



When reduced by concentrated hydrochloric acid and stannous chloride, it forms a colourless solution from which only a small amount of the hydrochloride of a base has been obtained. The action of diazotised *m*-toluidine on 2:4-diaminotoluene leads to the formation of a *diaminoazotoluene*, $\text{C}_7\text{H}_7\cdot\text{N}_2\cdot\text{C}_7\text{H}_5(\text{NH}_2)_2$, which crystallises from ethyl acetate, on addition of light petroleum, in small, dark cherry-red crystals. G. Y.

Diazo-ethers. HANS EULER (*Ber.*, 1903, 36, 3835—3837).—In spite of Hantzsch's communication (*Abstr.*, 1903, i, 869), the author is still of opinion that his experiments (*Abstr.*, 1903, i, 722) support Bamberger's view that the products of saponification of diazo-ethers are normal diazoxides. A. McK.

Aniline Bases and Nitrous Esters in Alkaline Solution. HANS EULER (*Ber.*, 1903, 36, 3837—3840. Compare preceding abstract).—It is supposed by Hantzsch that diazo-ethers decompose, under the conditions employed by Bamberger and by the author, into aniline base and nitrous ester, thus :



Hantzsch further holds that the coupling with β -naphthol observed by Bamberger and by the author was due to the presence of those decomposition products. The author now proves that those decomposition products do not couple with β -naphthol in alkaline solution.

Aniline was shaken with an aqueous solution of sodium hydroxide containing *isoamyl* nitrite on the one hand and methyl nitrite on the other. Those solutions, after being extracted with ether, did not couple with the β -naphthol solutions previously employed by the author (*Abstr.*, 1903, i, 722).

Hantzsch's views in this matter are, therefore, contradictory to facts. A. McK.

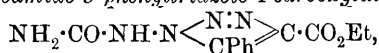
Colour of Aqueous Solutions of Methyl-orange and the Change which Acids produce in it. P. VAILLANT (*Compt. rend.*, 1903, 137, 849—851).—The well known colour change produced in yellow solutions of methyl-orange by the addition of acids has been explained in two ways. Ostwald (*Grundlagen der Anal. Chimie*, ch. 6) maintains that the red tint is due to the undissociated molecule whilst the anions of the dye give rise to the yellow colour. Küster (*Zeit. physikal. Chem.*, 1897, 13, 127) also supposes the yellow colour to be due to the anion, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3^-$, but assigns the red to the electrically neutral group $\text{H}\cdot\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3^-$, which is formed on bringing hydrogen ions into solutions containing the yellow anion. The author shows that neither of these hypotheses are in accordance with his observations. It was found that the molecular absorption of aqueous solutions of methyl-orange remains constant at

all dilutions in spite of varying dissociation. This fact seems to prove that both the undissociated molecule and anion gave the same colour, hence the colour changes produced by acids cannot be explained by dissociation. It is also shown that the absorption coefficient of aqueous solutions undergoes a great change when acids are added, an effect which varies in intensity with the strength of the acid. The author concludes that the molecule of methyl-orange undergoes a change in structure under the influence of acids, the product being red in colour. Red crystals were obtained by evaporating an acidified alcoholic solution of the dye (compare also Stieglitz, this vol., ii, 17).

S. S.

Diazoanhydrides and 1-Amino-1:2:3-triazole. LUDWIG WOLFF and A. A. HALL (*Ber.*, 1903, 36, 3612—3618).—The compounds formed by the condensation of diazoanhydrides with phenylhydrazine or semicarbazide (Wolff, *Abstr.*, 1903, i, 203) are derivatives of 1-aminotriazole. The primary triazole bases cannot be prepared by means of hydrazine under the same conditions, but result from the decomposition of the 1-carbamidotriazoles by acids.

The *anhydride* of ethyl diazobenzoylacetate, $O \left\langle \begin{smallmatrix} \text{CPh} \\ \text{N:N} \end{smallmatrix} \right\rangle \text{C} \cdot \text{CO}_2\text{Et}$, is obtained by the careful reduction of ethyl isonitrosobenzoylacetate, which may be prepared by the general method for these compounds (*loc. cit.*, Perkin, *Trans.*, 1885, 47, 244). The diazoanhydride is a yellow oil, dissolving in ether or alcohol but insoluble in water, and having a sp. gr. 1.2138 at 0°, very stable towards cold dilute acids or iodine, but decomposed by hot acids or alkalis. Semicarbazide forms ethyl 1-carbamido-5-phenyltriazole-4-carboxylate,



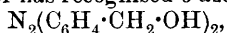
which crystallises from alcohol in bundles of needles melting at 208°, and dissolves in sodium carbonate, being reprecipitated by carbon dioxide. Sodium hydroxide hydrolyses it to the *carboxylic acid*, which forms a granular mass, melting and decomposing at 208°, dissolving sparingly in ether, hot alcohol, or water.

Carbamidomethyltriazolecarboxylic acid (*loc. cit.*) is decomposed by hydrochloric acid, forming aminomethyltriazolecarboxylic acid, which is best isolated by means of its *benzylidene* compound, $\text{C}_{11}\text{H}_{10}\text{O}_2\text{N}_4$, crystallising in colourless needles and melting and decomposing at 170°. Hot acids or alkali hydroxides hydrolyse it, forming 1-amino-5-methyltriazole-4-carboxylic acid, which crystallises from water in slender, colourless needles or prisms and decomposes at 190° into carbon dioxide and aminomethyltriazole. Solutions of the salts have no reducing action on Fehling's solution or ammoniacal silver nitrate in the cold. The acid condenses with a hot solution of acetaldehyde, forming a compound which crystallises in needles and melts and decomposes at 153°.

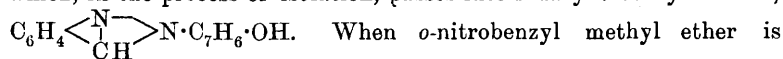
1-Benzylideneamino-5-methyltriazole, $\text{CHPh} \cdot \text{N} \cdot \text{N} \left\langle \begin{smallmatrix} \text{N:N} \\ \text{CMe} \end{smallmatrix} \right\rangle \text{CH}$, prepared by heating benzylideneaminomethyltriazolecarboxylic acid at about 200° until the evolution of carbon dioxide ceases, crystallises

from light petroleum in colourless prisms or tablets melting at 67—68°, and forms a *hydrochloride* which crystallises in needles and melts and decomposes at 135—140°. Hydrochloric acid hydrolyses the benzyldene derivative to benzaldehyde and 1-*amino-5-methyltriazole*, $\text{NH}_2 \cdot \text{N} \langle \begin{smallmatrix} \text{N} \cdot \text{N} \\ \text{CMe} \end{smallmatrix} \rangle \text{CH}$, which crystallises from benzene in colourless leaflets melting at 70° and dissolves readily in water, alcohol, or chloroform, less readily in ether. The solution has a neutral reaction, and reduces gold chloride on warming, but not Fehling's solution or ammoniacal silver nitrate. The *hydrochloride*, $\text{C}_3\text{H}_6\text{N}_4\text{HCl}$, crystallises from alcohol in colourless needles, which melt and decompose at 138°. The aqueous solution has an acid reaction and reduces Fehling's solution on heating. The *platinichloride* is yellow and granular, the *aurichloride* is oily. C. H. D.

Formation of Azo-compounds. Reduction of *o*-Nitrobenzyl Methyl Ether. PAUL FREUNDLER (*Compt. rend.*, 1903, 137, 521—523. Compare Abstr., 1903, i, 371).—In addition to the substances already detected (*loc. cit.*) among the reduction products of *o*-nitrobenzyl alcohol, the author has recognised *o*-azobenzyl alcohol,

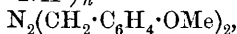


which, in the process of isolation, passes into indazyl-*o*-benzyl alcohol,

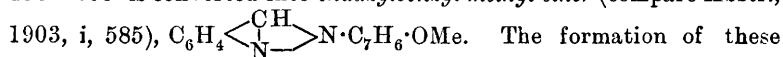


When *o*-nitrobenzyl methyl ether is reduced by zinc dust and sodium hydroxide in presence of alcohol, there are formed anthranilic acid, indazyl-*o*-benzoic acid (*loc. cit.*), *o*-aminobenzyl methyl ether, the *oxalate* of which melts at 124°, a yellow *resin* soluble in ether and acids, and having the properties of

benzylene-imine, $\left(\text{C}_6\text{H}_4 \langle \begin{smallmatrix} \text{CH}_2 \\ \text{NH} \end{smallmatrix} \rangle \right)_n$, and *o*-azobenzyl methyl ether,



which crystallises in red prisms, melts at 68·5°, and when heated at 150—200° is converted into *indazylbenzyl methyl ether* (compare Abstr.,



The formation of these substances indicates that the ether is first partially saponified by the sodium hydroxide. *o*-Nitrobenzyl ethyl ether furnishes similar products on reduction by this method. T. A. H.

Reduction Products of Azo-compounds. X. Reduction of Toluene-*o*-azophenetole and Bromobenzeneazophenetoles with Acid Reducing Agents. PAUL JACOBSON, GEORG FRANZ, and KARL ZAAR (*Ber.*, 1903, 36, 3857—3872. Compare Abstr., 1896, i, 23, 24, 27, 96; 1898, i, 440).—The products obtained by the reduction of toluene-*o*-azophenetole with tin chloride and hydrochloric acid have been reinvestigated, and it is now found that some 20 per cent. of an *o*-semidine is formed and may be separated by the formic acid method. The yield of *o*-semidine is better when Witt and Helmont's method (Abstr., 1894, i, 606) of reduction is adopted. The three bromobenzeneazophenetoles have also been reduced and they behave very similarly to the corresponding methyl compound. A table is given

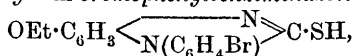
showing the amount of *o*- and *p*-semidines and decomposition products obtained from various substituted benzeneazophenetoles. A substituent in the positions 2 or 2' tends to diminish the amount of *o*-semidine and to increase the amount of *p*-semidine, although the influence is not so marked as first stated. A substituent in the position 3' also appears to diminish the amount of *o*-semidine and it appears questionable whether the lessening of *o*-semidine formation is to be attributed to steric influences.

2-Amino-5-ethoxy-2'-methyldiphenylamine, obtained from toluene-*o*-azophenetole by Witt and Helmont's process, crystallises from light petroleum in colourless plates melting at 82—83°. It reacts with nitrous acid and gives the characteristic azimide formation. Boiling with formic acid converts the base into 6-ethoxy-1-*o*-tolylbenziminazole, $\text{OEt} \cdot \text{C}_6\text{H}_3 \langle \text{N} \text{---} \text{CPh} \rangle \text{CH}$, which crystallises in needles melting at 77—78°. The stilbazonium base, $\text{OEt} \cdot \text{C}_6\text{H}_3 \langle \text{N} = \text{CPh} \rangle \text{CPh} \cdot \text{OH}$ (compare Kehrman and Woulfson, Abstr., 1899, i, 506; Hantzsch and Kalb, 1900, i, 114), crystallises in yellow plates melting at 172°.

The diformyl derivative of the *p*-semidine, $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{CHO}) \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NH} \cdot \text{CHO}$ [$\text{OEt} : \text{Me} : \text{NH} = 4 : 3' : 4'$], crystallises from dilute alcohol in prisms melting at 140°.

In the preparation of *o*-bromobenzeneazophenol (Hewitt, Moore and Pitt, Abstr., 1898, i, 653), a hydroxybenzenebisazo-*o*-bromobenzene, $(\text{C}_6\text{H}_4\text{Br} \cdot \text{N}_2)_2 \cdot \text{C}_6\text{H}_3 \cdot \text{OH}$, is formed. It crystallises in reddish-brown plates, melts at 160°, and is readily soluble in benzene or acetic acid. *o*-Bromobenzeneazophenetole crystallises from alcohol in yellowish-red plates, melts at 39°, and is readily soluble in most solvents. When reduced by Witt's process it yields a *p*-semidine, 3-bromo-4-amino-4'-ethoxydiphenylamine, $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{NH}_2$, in the form of colourless plates melting at 54°. The hydrochloride and sulphate are both sparingly soluble, and the *m*-nitrobenzylidene derivative melts at 137—138°. An *o*-semidine is also formed during the reduction and may be isolated in the form of its methylene compound, 6-ethoxy-1-*o*-bromophenylbenziminazole, the picrate of which melts at 176°.

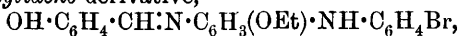
m-Bromobenzeneazophenol melts at 139—140° (Hewitt, 136°) and the ethyl ether at 68°. Hydroxyphenylbisazo-*m*-bromobenzene crystallises in needles and melts at 162—163°. 3'-Bromo-2-amino-5-ethoxydiphenylamine yields a crystalline hydrochloride, condenses with benzil to form 2-hydroxy-7-ethoxy-1-*m*-bromophenyl-2 : 3-diphenyl-1 : 2-dihydroquinoxaline, $\text{OEt} \cdot \text{C}_6\text{H}_3 \langle \text{N} = \text{CPh} \rangle \text{CPh} \cdot \text{OH}$, in the form of yellow crystals melting at 166—169°. With carbon disulphide, it yields 2-thiol-6-ethoxy-1-*m*-bromophenylbenziminazole,



which crystallises in colourless needles melting at 201°.

6-Ethoxy-1-*m*-bromophenylbenziminazole, $\text{OEt} \cdot \text{C}_6\text{H}_3 \langle \text{N} \text{---} \text{C} \rangle \text{CH}$, crystallises in colourless needles and melts at 130°; the picrate forms

yellow needles and melts at 220—221°. The *o*-semidine yields an *o*-hydroxybenzylidene derivative,



melting at 116°.

J. J. S.

Azo-compounds from Aziminonaphthalenesulphonic Acids. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 139908 and 143387).—Azo-dyes prepared from diazotised *o*-aminophenols and 1:8-diaminonaphthalene-4-sulphonic acid react with hydrochloric acid and sodium nitrite, forming azo-compounds of 1:8-aziminonaphthalene-4-sulphonic acid. *p*-Nitro-*o*-aminophenol, picramic acid, and 6-nitro-2-aminophenol-4-sulphonic acid yield suitable diazonium compounds. The same dyes may also be prepared by the direct combination of the diazonium compounds with 1:8-aziminonaphthalene-4-sulphonic acid.

C. H. D.

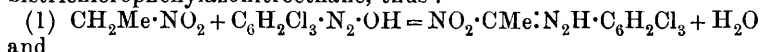
Solid Azo-dyes derived from 1-Aminoanthraquinone. CHARLES LAUTH (*Compt. rend.*, 1903, 137, 661—664).—1-Diazoanthraquinone combines readily with amines and phenols and their sulphonic acid derivatives to form solid, soluble dyes, rich in colour; those derived from the naphtholsulphonic acids and aminonaphtholsulphonic acids are not affected by light, and resist the process of fulling. Anthraquinoneazo- β -naphthol-8-sulphonic acid is a *red* dye, which can be employed in the presence of chromic acid to obtain mixed dyes; similar dyes are afforded by β -naphthol-6-sulphonic acid, β -naphthol-3:7-disulphonic acid, β -naphthol-3:8-disulphonic acid, β -naphthol-7-sulphonic acid, and naphthionic acid.

Amaranth dyes are afforded by Piria's salt (α -naphtholsulphonic acid) and "chromotrope" acid (1:8-dihydroxynaphthalene-3:6-disulphonic acid); *violet* dyes by α -naphthylamine and 8-amino- α -naphthol-3:6-disulphonic acid; and *brown* dyes by α -naphthol, resorcinol, *m*-aminophenol, *o*- and *m*-cresotic acids, β -naphthylamine-6-sulphonic acid (Brönner's salt), tolylenediamine, β -naphthylamine, diphenylamine, and salicylic acid.

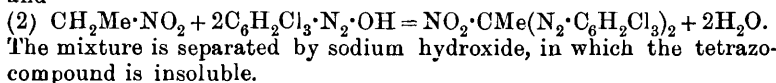
The sulphonic acid derivatives of 1-diazoanthraquinone give similar series of azo-dyes, which are more soluble in water than those already described.

M. A. W.

Mixed Tetrazo-compounds. EUGEN BAMBERGER and JOHANNES FREI (*Ber.*, 1903, 36, 3833—3835).—It is known that nitroparaffins, like phenols, interact with diazonium salts to form hydrazones. Diazotised *s*-trichloroaniline acts on nitroethane to form a mixture of nitroacetaldehyde trichlorophenylhydrazone and the mixed tetrazo-compound, bistrichlorophenylazonitroethane, thus:



and



Bis-2:2:4-trichlorophenylazonitroethane separates from acetone in tiny needles and melts at 97.5°.

Bis-2:2:4-tribromophenylazonitroethane, prepared from nitroethane

and tribromodiazobenzene, forms ochre-coloured crystals which melt and decompose at 98°.

Nitroacetaldehyde-2 : 2 : 4-tribromophenylhydrazone separates from alcohol in golden-yellow, glistening leaflets and melts at 116—117°.

A. McK.

1-Phenyl-3-methylpyrazole-4-azobenzene. AUGUST MICHAELIS and R. LEONHARDT (*Ber.*, 1903, **36**, 3597—3599).—5-*Chloro-1-phenyl-*

3-methylpyrazole-4-azobenzene, $\text{N} \begin{smallmatrix} \text{NPh} \cdot \text{CCl} \\ \text{CMe} \cdot \text{C} \cdot \text{N} \cdot \text{NPh} \end{smallmatrix}$, prepared by heating phenylmethylpyrazolone-azobenzene with phosphorus oxychloride at 120°, crystallises from hot alcohol in slender, yellow needles, melts at 190°, and has feeble basic properties, but does not combine with methyl iodide; the chlorine is not eliminated by aqueous or alcoholic potash, but the compound can be readily reduced in alkaline solution.

1-Phenyl-3-methylpyrazole-4-azobenzene, $\text{N} \begin{smallmatrix} \text{NPh} \cdot \text{CH} \\ \text{CMe} \cdot \text{C} \cdot \text{N} \cdot \text{NPh} \end{smallmatrix}$, prepared by the action of zinc dust and sodium hydroxide on the preceding compound, crystallises from alcohol in small, reddish-yellow flakes, melts at 126°, and is isomeric with the compound described by Beyer and Claisen (*Abstr.*, 1888, 827); it crystallises unchanged from hydrochloric acid, is insoluble in alkalis, and appears to be reduced to the colourless hydrazo-compound by tin and hydrochloric acid.

T. M. L.

Precipitation of Colloids. KARL SPIRO (*Beitr. chem. Physiol. Path.*, 1903, **4**, 300—322. Compare Pauli, *Abstr.*, 1902, ii, 388; 1903, i, 299).—There is no radical difference between the precipitation of colloids and proteids by neutral salts or by alcohols. The action of various salts is quite different and depends both on the metallic and acid radicle present, and also on the nature of the colloidal substance. The concentration of the solution is also an important factor, as more highly concentrated solutions are more readily precipitated than dilute ones.

The process of “salting out” is not merely a withdrawal of the solvent depending on the amount of the precipitating agent employed. In the typical case of “salting out” of a proteid, two layers are always formed, each of which contains the three substances, proteid, salt, water, but with different concentrations. The upper layer contains much water and salt, and only a little proteid, the lower contains much proteid and only little salt and water. For different temperatures, the ratio of water to salt in the precipitated layer may be the same, but the ratio of salt to proteid is not, and hence the precipitate is not a compound of the proteid and salt.

With solutions of gelatin, it has been found that the higher the concentration of the salt solution the less water does the gelatin layer contain and, on the other hand, the aqueous layer becomes poorer in gelatin. The method of salting is therefore a workable method for separating proteids and gives quantitative results, which are better than those obtained by such processes as that of ether extraction.

The partition coefficient does not merely depend on the solubility,

but also on a factor termed the "solubility intensity" (the intensity with which, for example, salt and water combine is greater than that of proteid and water). The solution pressure is thus not merely influenced by the osmotic pressure, but also by the solubility intensity.

The temperature of coagulation of albumin solutions is reduced by the introduction of monohydric alcohols of the fatty series, and the greater the amount of alcohol present the lower is the temperature. The lower homologues are not so effective as the higher alcohols.

Polyhydric alcohols (glycerol, mannitol, &c.) retard coagulation and render the coagulation less complete. Phenols produce precipitation, but even with excess of phenol, this is not complete. With resorcinol, the precipitation does not occur so readily, and on the addition of 45 per cent. of the phenol the original precipitate redissolves.

A solution of potassium acetate completely inhibits precipitation of albumin. Other salts, for example, calcium, magnesium, zinc, and mercuric chlorides, mercuric acetate, and potassium thiocyanate dissolved in methyl, ethyl, or isopropyl alcohol have the same effect.

Methyl and ethyl alcohols are not capable of precipitating colloidal ferric oxide, but propyl alcohol is, as is also amyl alcohol when its concentration is increased by the addition of methyl alcohol. For aqueous calcium chloride and ferric oxide solutions, the lower limit of precipitation (that is, the amount of calcium chloride required to produce opalescence) is constant if the concentration remains constant, but increases with an addition of water. The addition of methyl alcohol to the oxide solution increases the absolute amount of calcium chloride required, but the precipitation limit remains the same. J. J. S.

Tryptophan Reaction of Various Proteids. THOMAS B. OSBORNE and ISAAC F. HARRIS (*J. Amer. Chem. Soc.*, 1903, 25, 853—855. Compare Abstr., 1903, i, 872).—The results are given of the application of the Hopkins-Cole reagent (Abstr., 1901, i, 310) to a number of vegetable proteids. In most instances, a positive reaction was obtained, but in the case of zein from maize only a very slight, transitory coloration was produced. The alcohol-soluble proteids of the oat and barley malt yielded a brown coloration which rendered the test inconclusive. The marked difference in the intensity of the reaction with different proteids indicates that the proportion of tryptophan yielded by the several proteids differs considerably. E. G.

Sulphur in Gelatin. OTTO KRUMMACHER (*Zeit. Biol.*, 1903, 45, 310—323).—In commercial gelatin, the total percentage of sulphur found was 0.62; in purified material, 0.28. The percentage of sulphur as sulphate and sulphite respectively in commercial gelatin was 0.36 and 0.04; in pure gelatin, 0.01 and 0.01 (?). Examples are given of the method of estimating sulphur by the use of Mahler's calorimetric bomb. W. D. H.

Animal Glutins. I. Sinew Glutin. WL. S. SADIKOFF (*Zeit. physiol. Chem.*, 1903, 39, 396—410).—A glutin has been obtained from sinews of cattle by three methods, namely, (a) by Van Name's

method, in which proteid impurities are fermented by the aid of trypsin; (b) by the repeated action of 0.25 per cent. potassium hydroxide solution; (c) by treatment for a short time with 0.25 per cent. potassium hydroxide, and, after washing with water, with 0.25 per cent. sodium carbonate solution.

The mean results of various analyses are: C, 50.90; H, 6.80; N, 18.2 (Kjeldahl's method) or 18.59 (Dumas' method); S, 0.34 to 0.5. These numbers agree very well with those obtained by Paal (Abstr., 1892, 895) and by Sadikoff for gelatin.

The glutin obtained by the first method exists in a form (A) which is sparingly soluble in cold water, but which dissolves readily in warm water and readily gelatinises, and also in a form (B) which is readily soluble in cold water, but the solution so obtained does not readily gelatinise. Somewhat similar modified forms have been obtained by the second method, but the differences are not shown in the results of analysis.

J. J. S.

Animal Glutins. II. Cartilage-glutins (Gluteins). WL. S. SADIKOFF (*Zeit. physiol. Chem.*, 1903, 39, 411—422. Compare Mörner, Abstr., 1889, 736).—Cartilage-glutin from the pig's nasal membrane, from cattle, and from the elastic tissue from the muscle of the pig's ears, has been prepared and analysed. All specimens contain less carbon and nitrogen and more sulphur than sinew glutin. Low results are obtained for nitrogen when determined by the Kjeldahl method. After hydrolysis with acids, the glutins have only a feeble reducing action on alkaline cupric oxide solutions. They all give a reaction with hydrochloric acid and phloroglucinol in the presence of alcohol. In these respects, they differ from sinew glutin and from commercial gelatin.

Treatment of the cartilage for a short time with dilute hydrochloric acid (0.2 per cent.) renders it soluble in water and alters the composition, the carbon and hydrogen becoming higher and the nitrogen lower.

J. J. S.

Plastein of Egg-albumin. D. KURAÉEFF (*Beitr. chem. Physiol. Path.*, 1903, 4, 476—485. Compare Abstr., 1902, i, 731).—Plastein was obtained by the digestion of crystalline egg-albumin with gastric juice and subsequent addition of rennet to the albumose solution so obtained. Elementary analyses of two preparations are given. A change of the plastein-albumoses into coagulable proteid by the gastric mucous membrane is probable, but the results are not very conclusive.

W. D. H.

Preparation and Analysis of Nucleic Acids. VI. PHOEBUS A. LEVENE (*Zeit. physiol. Chem.*, 1903, 39, 479—483. Compare Abstr., 1901, i, 299, 300, 623; 1903, i, 668, 779; ii, 438).—A nucleic acid has been obtained from the testicles of oxen by the usual methods. It did not give the biuret and Millon's reactions, and did not reduce Fehling's solution after having been warmed for a short time with mineral acids. On hydrolysis with 1 per cent. sulphuric acid at 125°,

it gave guanine and adenine, and with 25 per cent. sulphuric acid at 150—175° thymine and cytosine.

A similar nucleic acid has been obtained from the brains of oxen. On hydrolysis with sulphuric acid, it gives the purine and pyrimidine bases already mentioned.
J. J. S.

Oxidation of Thymonucleic Acid with Calcium Permanganate. FRIEDRICH KUTSCHER and JOHN SEEMANN (*Ber.*, 1903, 36, 3023).—When thymonucleic acid is oxidised with calcium permanganate in feebly alkaline solution, it yields carbamide and guanidine, but not uric acid; the amount of guanidine produced corresponds with the presence in the original material of 5 per cent. of guanine.
T. M. L.

Thymonucleic Acid. S. KOSTYTSCHEW (*Zeit. physiol. Chem.*, 1903, 39, 545—560).—Neumann's α - and β -nucleic acids (*Abstr.*, 1899, i, 467; 1900, i, 319) are not pure compounds, but are mixtures in different proportions of two acids called α - and β -nucleic acids by the author. For the preparation of the pure α -acid, Neumann's α -acid is transformed into its barium salt, and this is treated with excess of barium acetate when a gelatinous precipitate is obtained. The solution and precipitation are repeated 3 times and the pure barium salt is then dissolved in warm water, cooled to 40°, and precipitated with methyl alcohol. This operation is repeated a second time, and the product then thoroughly washed with methyl alcohol and ether. The barium salt has the composition $C_{41}H_{70}O_{26}N_{14}P_4Ba_2$, and the free α -acid, $(C_{41}H_{74}O_{26}N_{14}P_4)_n$. Solutions of the sodium and barium salts are readily gelatinised, or yield gelatinous precipitates on the addition of a number of solutions of different metallic salts. The addition of alkalis or acids, or boiling for a short time, dissolves the gelatinous material. The β -acid, obtained from Neumann's β -acid by removal of the α -acid as its barium salt, yields salts which do not gelatinise. The barium salt has the composition

$C_{90}H_{141}O_{61}N_{27}P_{10}Ba_6$,
and the free acid, $C_{90}H_{153}O_{61}N_{27}P_{10}$. The β -acid, when hydrolysed with sulphuric acid and mercuric sulphate, yields about one-third as much nucleic bases as can be obtained from the same weight of the α -acid.
J. J. S.

Chemical Investigations on Lymphatic Organs. II. Constitution of Natural Histon Nucleate. IVOR BANG (*Beitr. chem. Physiol. Path.*, 1903, 4, 331—361. Compare *Abstr.*, 1899, i, 836; 1901, i, 57, 299; 1902, ii, 36; 1903, ii, 664, 739).—When a solution of histon nucleate (nucleohiston) is saturated with sodium chloride, a precipitate of histon is obtained; the addition of alcohol to the filtrate precipitates the nucleic acid, but the clear solution still gives the biuret reaction. This is due to the presence of parahiston (Fleroff, *Abstr.*, 1900, i, 71) in the filtrate.

According to the author, Malengreau's A- and B-histons are essentially the same compound; the reason that they give somewhat different reactions is attributed to the presence of small amounts of impurities.

Recent researches have proved that, of the five reactions described (Abstr., 1899, i, 836) as characteristic of histons, only the fourth and fifth apply generally. The histons are now placed in a special group with the protamines on account of the similarity in the properties.

Solutions of the alkali salts of the nucleic acid are not precipitated on the addition of saturated sodium chloride solution, but the addition of a few drops of acetic acid causes the immediate precipitation of the whole of the nucleic acid in the form of an acid salt.

The composition of the normal sodium salt is practically the same as that of salmonnucleic acid, namely, $C_{40}H_{52}O_{26}N_{14}P_4Na_4$. When hydrolysed with 5 per cent. sulphuric acid, it yields xanthine, hypoxanthine, guanine, adenine, thymine, cytosine, lævulic acid, and formic acid, but not glycuronic acid. On distillation with magnesia, ammonia is not formed.

The acid presumably consists of two distinct nucleic acids, normal nucleic acid ($\frac{2}{3}$), and adenylic acid ($\frac{1}{3}$). Experiments lead to the conclusion that the original histon nucleate is made up of histon combined with the normal acid and parahiston combined with the adenylic acid. The two salts probably form a double compound as the original substance does not vary in composition. The formula $C_{765}H_{1188}O_{342}N_{252}S_3P_{36}$ for the double compound is suggested.

The molecular weight of histon is calculated as 6122, and that of parahiston as 3060. The author's view is that the histon nucleate exists preformed in the thymus cell, but probably as part of a much larger molecule.

Histon itself forms a neutral and an acid chloride; the former precipitates proteids, but the latter does not. Histon nucleate also has acidic properties and forms alkali salts, and is capable of combining with proteids. The solubility of histon salts tends to decrease as the basicity of the acid with which the histon is combined increases.

Some 31 per cent. of the total phosphorus present in thymus cells exists in the form of histon nucleate. The nucleate has no coagulating properties.

J. J. S.

Ovimucoid and Serum-mucoid. II. CARLO U. ZANETTI (*Gazzetta*, 1903, 33, i, 160—164. Compare Abstr., 1899, i, 180).—Like ovimucoid (*loc. cit.*), serum-mucoid, prepared from the serum of ox-blood, yields glucosamine on hydrolysis with hydrochloric acid.

T. H. P.

Adrenalin. HERMANN PAULY (*Ber.*, 1903, 36, 2944—2949. Compare Takamine, Abstr., 1902, ii, 217; 1903, i, 376; Aldrich, Abstr., 1901, ii, 564; Abel, Abstr., 1903 i, 376; von Fürth, *ibid.*, i, 669).—The analyses of adrenalin agree best with Aldrich's formula, $C_9H_{13}O_3N$. It is optically active, and has $[\alpha]_D - 43^\circ$ at 23.5° . It is considered highly improbable that adrenalin contains a C:N group in the side chain, but rather that it is a secondary base containing the grouping $OH \cdot CH \cdot CH_2 \cdot NHMe$ or $OH \cdot CH_2 \cdot CH \cdot NHMe$.

J. J. S.

Influence of Electrolytes on Enzymes. II. On Invertin. SYDNEY W. COLE (*J. Physiol.*, 1903, 30, 281—289).—The results

obtained justify the conclusion that electrolytes exert their effect by an influence on the ferment itself and not on the substrate, for it is in the highest degree improbable that starch and cane-sugar would respond in the same way to the addition of electrolytes.

W. D. H.

Action of Alcohol and Acids on Enzymes. THOMAS BOKORNY (*Milch.-Zeit.*, 1903, 32, 641—642).—The results of a number of experiments on the sensitiveness of enzymes towards alcohol and acids are given. Zymase is destroyed by absolute alcohol within a few minutes, and is, after a time, affected by even a 10 per cent. solution of alcohol. On the other hand, invertase still retains its inverting action after being treated for 20 days with absolute alcohol. Maltase is remarkably sensitive, its action being inhibited by dilute alcohol. Lactase is not affected by 10 per cent. alcohol,

The presence of 0.1 per cent. of sulphuric acid destroyed the action of zymase, when allowed to act on it for 5 days. 0.02 per cent. of the same acid at the ordinary temperature also had an injurious action, and destroyed the enzyme at 40°. 0.5 per cent. of lactic acid practically stopped the fermenting action of yeast within 4 days, but had no influence on lactase (compare Abstr., 1903, ii, 324).

W. P. S.

Proteolytic Enzymes. REGINALD O. HERZOG (*Zeit. physiol. Chem.*, 1903, 39, 305—312).—Proteolytic enzymes (pepsin, trypsin, papain) increase the viscosity of concentrated solutions of proteolytic products. This is inhibited by the addition of the juice expressed from *Ascaris*; although the action does not occur if the juice has been previously boiled. The increase of viscosity is believed to be due to the reversed action of the enzymes, and is analogous to the plastein formation noted by others. The action of rennet is not inhibited by *Ascaris* juice.

W. D. H.

Action of Oxidising Enzymes on Carbohydrates. NADINE SIEBER (*Zeit. physiol. Chem.*, 1903, 39, 484—512).—Three oxidising enzymes (oxydases) have been obtained from the plasmafibrin of horses' blood and from other animals. Of the three enzymes, one is soluble in water, another soluble in neutral saline solution, and the third readily soluble in water and alcohol.

The normal blood plasma of horses or the plasma from horses inoculated against bubonic plague contain little or no oxydase soluble in water. It is most readily obtained from animals inoculated against diphtheria, streptococci, and staphylococci. The oxydase may be precipitated from its aqueous solution by the aid of carbon dioxide or ammonium sulphate. Its aqueous emulsion reacts with guaiacol and other reagents for detecting oxidising substances; it further gives most of the reactions characteristic of proteids. Its oxidising power begins to diminish after heating for 5 minutes at 70°. All three enzymes may be kept for some time in the dark and in the presence of thymol.

To obtain the second oxydase, the fibrin, after treatment with distilled water, is extracted with an 8 per cent. potassium nitrate solution in a thermostat. It can be precipitated by the addition of carbon dioxide, alcohol, or ammonium sulphate and purified by dialysis. It has been obtained from the fibrin of all blood sera examined and gives reactions similar to those obtained with the oxydase soluble in water, except that it gives no coloration with tincture of guaiacum in presence of hydrogen peroxide. Heating at 65° for 5 minutes tends to destroy its oxidising properties. The third oxydase, which can only oxidise in the presence of hydrogen peroxide, may be obtained from the mother liquors of the second oxydase. These are concentrated at temperatures not above 37° and all ammonium sulphate removed by the addition of alcohol. Its solution may be heated at 90° for some minutes without impairing the oxidising power to any considerable extent.

All three oxydases are capable of decomposing aqueous solutions of dextrose. After 3 days, from 80—90 per cent. of the carbohydrate has disappeared and carbon dioxide has been formed. It is also found that part of the oxygen in the air above the solution is used up, although in the case of the oxydase soluble in water the amount is but small.

When the solution of the first oxydase is heated to 100°, its activity is not completely destroyed. The three enzymes do not react so readily with solutions of sucrose, and they vary as regards their relative activities, the oxydase soluble in neutral salts yielding the largest amount of carbon dioxide and further yielding dextrose (confirmed by the formation of osazone).

The oxydase soluble in water is the most active as regards the decomposition of starch.

Oxydases from vegetable sources are also capable of inducing similar decompositions.

J. J. S.

Formation of Hydrogen Sulphide by Organic Extracts and Proteids. M. EMMANUEL POZZI-ESCOT (*Compt. rend.*, 1903, 137, 495—496).—When powdered sulphur or sodium hydrogen sulphite is added to an aqueous extract of yeast preserved with chloroform or sodium fluoride, hydrogen sulphide is evolved. This action does not occur unless sulphur or a sulphite is added, and is inhibited by previously boiling the extract; it must therefore be due to the activity of a reductase present in the yeast.

T. A. H.

Action of Aniline Dyes on Invertin. S. S. MERESHKOWSKY (*Centr. Bakt. Par.*, 1903, 11, 33—45).—The action of magenta, Congo-red, and safranine respectively on invertin has been examined. A small amount of magenta does not affect the action of invertin on sucrose, whilst a larger amount entirely prevents the inversion of the sugar. Congo-red, in the proportion of one part to 1000 of solution, has no effect on invertin. The fermenting action of yeast is impaired by the presence of magenta.

Apparently invertin is not destroyed in the presence of solutions of the dyes below a certain concentration, but it forms an unstable compound with the dye. The addition of fresh sugar solution then

destroys this compound and liberates a part at least, if not the whole, of the invertin. A. McK.

Influence of Electrolytes on Amylolytic Ferments. SYDNEY W. COLE (*J. Physiol.*, 1903, 30, 202—220).—The action of dialysed ptyalin on dialysed starch is increased by the addition of very small amounts of acids and of neutral salts of strong monobasic acids. The action is decreased by the addition of large amounts of acid (0·0007 to 0·0012 per cent. of hydrochloric), and by neutral salts of weak monobasic, dibasic, and tribasic acids. The explanation advanced is that the presence of anions other than those of hydroxyl accelerates, and the presence of cations and hydroxyl ions depresses, the activity of the enzyme. In adding an acid, there are thus two factors introduced, and the effect of various strengths of acid depends on the preponderating influence of one or the other. W. D. H.

Lipase. MAURICE DOYEN (*Compt. rend. Soc. Biol.*, 1903, 55, 1209—1211).—Polemical against Hanriot. W. D. H.

Action of Fluorescent Substances on Ferments and Toxins. HERMANN VON TAPPEINER (*Ber.*, 1903, 36, 3035—3038).—The poisonous action of fluorescent substances on infusoria is enormously intensified by the influence of light (Tappeiner and Raab, *Münch. med. Woch.*, 1900, 1). The effect of fluorescent substances on enzymes and toxins has accordingly been studied.

The conversion of starch into maltose by means of diastase is considerably retarded when eosin is present and when the solution is exposed to ordinary daylight. In the dark, eosin does not retard the formation of maltose, nor was the observed retarding effect due to the action of daylight alone. Magdala-red behaves like eosin, whilst the effect of quinoline-red is fainter than that of either eosin or Magdala-red. Acridine, dimethylphosphine, uranin, gallein, resorcinol-blue and æsculin have no action. Apparently only those fluorescent substances act, the light absorption of which lies in the green or light blue part of the spectrum. The effect is quite marked even when eosin, in the proportion of 1 : 400,000, is used.

The behaviour with invertin was analogous to that with diastase; with papayotin, a faint action was obtained by uranin and a very faint action by dimethylphosphine, whilst eosin, Magdala-red, and quinoline-red acted as with diastase and invertin.

When a solution containing ricin and a little eosin is exposed for 14 hours to diffused daylight, the ricin loses its characteristic property of coagulating red blood corpuscles; a solution containing ricin, in the absence of eosin, was unaltered in diffused daylight, whilst a solution containing both ricin and eosin was unaltered in the dark. By experiments on guinea-pigs, it was proved that the poisonous effect of a solution containing both eosin and ricin, which had been exposed to light, was less than that of a similar solution which had been kept in the dark. Uranin behaves similarly to eosin, but the action of Magdala-red, quinoline-red, and harmalin is somewhat fainter; the feeblest effect is that produced by dimethylphosphine. A. McK.

[Mercuric Derivatives of Sodium β -Naphtholsulphonates.] AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 143448 and 143726).—When sodium carbonate is added to a solution of sodium β -naphthol-6-sulphonate and mercuric chloride, a precipitate of the compound, $\text{NaSO}_3 \cdot \text{C}_{10}\text{H}_6\text{O} \cdot \text{HgCl}$, is obtained, separating from hot water as a colourless powder.

When sodium carbonate is added to a solution of sodium β -naphthol-3:6-disulphonate, and mercuric chloride is then added in the form of powder or concentrated solution, the clear solution obtained gradually deposits crystals of a mercuric compound, containing 32 per cent. of mercury.

The aqueous solutions of these compounds do not exhibit the characteristic reactions of the mercuric ion. C. H. D.

Silicon Compounds. III. WALTHER DILTHEY (*Ber.*, 1903, 36, 3207—3213. Compare *Abstr.*, 1903, i, 405, 591).—*Tri-dibenzoylmethylsilicon chloride hydrochloride*, $\text{Si}(\text{CHBz}_2)_3\text{Cl} \cdot \text{HCl}$, forms yellow needles, which lose hydrogen chloride on exposure to air, forming the compound $\text{Si}(\text{CHBz}_2)_3\text{Cl}$, already described. The solution in pyridine or sodium carbonate is colourless, unlike that of the acetyl-acetonyl and benzoylacetyl compounds, but a yellow colour is obtained on adding alcoholic potassium hydroxide to a solution of the chloride in absolute alcohol.

Dibenzoylmethane reacts with silicon bromide in chloroform solution, forming the *bromide-hydrobromide*, $\text{Si}(\text{CHBz}_2)_3\text{Br} \cdot \text{HBr}$, which crystallises in brown needles, insoluble in ether or benzene, but dissolving in glacial acetic acid with loss of $\frac{1}{2}\text{HBr}$. On prolonged boiling with acetic acid it yields the *bromide*, $\text{Si}(\text{CHBz}_2)_3\text{Br}$, which forms opalescent plates resembling the chloride. Bromine forms the *compound*, $\text{Si}(\text{CBrBz}_2)_3\text{Br} \cdot \frac{1}{2}\text{HBr}$, which crystallises in yellow needles, and is also obtained from bromodibenzoylmethane and silicon bromide. The *iodide*, $\text{Si}(\text{CHBz}_2)_3\text{I}$, is prepared by passing hydrogen iodide into a solution of the chloride in acetic acid, and forms stable, brownish-yellow leaflets, insoluble in ether or benzene, dissolving readily in chloroform or hot glacial acetic acid. Iodine forms brown leaflets of the *periodide*, $\text{Si}(\text{CHBz}_2)_3\text{I}_3$, which is insoluble in hot glacial acetic acid. Chloroform removes the added iodine. Picric acid reacts with the chloride in boiling chloroform solution, forming the *picrate*, $\text{Si}(\text{CHBz}_2)_3 \cdot \text{C}_6\text{H}_2\text{O}_2\text{N}_2$, crystallising from chloroform on addition of acetic acid and ether in yellow needles melting at 252—253°. The *hydrogen sulphate*, $\text{Si}(\text{CHBz}_2)_3 \cdot \text{HSO}_4$, crystallises from acetic acid-ether in thick, yellow prisms melting at 242°. The *nitrate* forms yellow prisms melting at 215°. With an excess of silver nitrate, the *double salt*, $2\text{Si}(\text{CHBz}_2)_3 \cdot \text{NO}_3 \cdot \text{AgNO}_3$, is formed, crystallising in silvery needles, decomposing at 180—181°, and blackening on exposure to light. C. H. D.

Organic Chemistry.

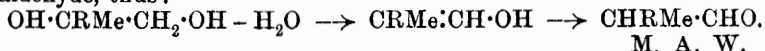
Action of Organo-magnesium Compounds on Acetylcarbinol and its Esters. ANDRÉ KLING (*Bull. Soc. chim.*, 1904, [iii], 31, 16—19).—Acetylcarbinyl acetate (1 mol.) and magnesium ethyl bromide (1 mol.) react in presence of anhydrous ether to give methyl-diethylcarbinol and the monoacetin of β -methylbutylene $\alpha\beta$ -glycol.

Acetylcarbinyl benzoate (1 mol.) and magnesium ethyl bromide (4 mols.) give phenyldiethylcarbinol, magnesium benzoate and β -methylbutylene $\alpha\beta$ -glycol, which boils at 188—189° under 760 mm. pressure.

Acetylcarbinol (1 mol.) and magnesium ethyl bromide (2 mols.) give β -methylbutylene $\alpha\beta$ -glycol. These facts show that the esters of acetylcarbinyl behave as ketones; anhydrous acetylcarbinol reacts as a ketone, and would therefore seem to have a different constitution from that contained in solution. S. S.

Transformation of Primary α -Glycols into the Corresponding Aldehydes. MARC TIFFENEAU (*Compt. rend.*, 1903, 137, 1260—1262).—The conversion of α -primary glycols into the corresponding aldehydes by the action of sulphuric acid, first observed by Zincke in the case of α -phenylethane- $\alpha\beta$ -diol, is a general reaction for primary substituted glycols. β -Phenylpropane- $\alpha\beta$ -diol, melting at 38°, and β -*p*-tolylpropane- $\alpha\beta$ -diol, melting at 36°, prepared by the action of magnesium methyl iodide on benzoylcarbinol and *p*-toluoylcarbinol respectively (compare Abstr., 1902, i, 433, and Kling, this vol., i, 2), lose a molecule of water on being heated with sulphuric acid (1:4), and are transformed into the corresponding aldehydes; β -phenylpropane- $\alpha\beta$ -diol yielding hydratropaldehyde, boiling at 204°, and forming a semicarbazide melting at 156—157° (compare Abstr., 1902, i, 666), and β -*p*-tolylpropane- $\alpha\beta$ -diol giving *p*-methylhydratropaldehyde, boiling at 219—221°, and forming a semicarbazide melting at 152°.

Since the glycol is converted into the aldehyde without change of structure, the author assumes that an intermediate vinyl alcohol is formed, which by the migration of a hydrogen atom passes into the aldehyde, thus:



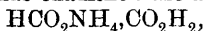
Esterification of Phosphoric Acid by Glycerol. PAUL CARRÉ (*Compt. rend.*, 1903, 137, 1070—1073).—Phosphoric acid reacts with glycerol under the ordinary and also under reduced pressure to form three esters, containing respectively one, two, and three glyceryl residues; the first is monobasic towards helianthin and dibasic towards phenolphthalein, the second is monobasic towards both indicators, whilst the third is neutral to indicators.

At a temperature of 105° under atmospheric pressure, the chief

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product is the mono-ester (35 per cent. of the phosphoric acid taken); the di-ester is also formed, the quantity reaching 6—7 per cent. when the heating is extended over 80 hours (compare Imbert and Belugou, *Abstr.*, 1900, i, 130). Under atmospheric pressure at 125°, a small quantity of the tri-ester is formed; the amount increases as the pressure is diminished, until at a temperature of 115° under 0.01 mm. pressure it is the only product, and corresponds with 98.8 per cent. of the phosphoric acid taken. M. A. W.

Solubility of Salts. XII. Ammonium Hydrogen Formate. ERICH GROSCHUFF (*Ber.*, 1903, 36, 4351—4357).—According to Reik (*Abstr.*, 1903, i, 308), ammonium formate does not yield an acid salt. The author having found (*ibid.*, i, 600) that potassium and sodium form hydrogen formates, has examined the ammonium salt,



which is prepared by dissolving the normal salt in glacial formic acid and cooling to 0°. The crystalline salt decomposes at 23° into formic acid and the normal salt. Water begins to decompose it at 9—10°. The solubility of the normal salt in water is increased by the addition of formic acid. C. H. D.

Acetates of the Alkaline Earths. ALBERT COLSON (*Compt. rend.*, 1903, 137, 1061—1063. Compare *Abstr.*, 1903, i, 396, 456, 601; this vol., i, 3).—A mixture of glacial acetic acid and acetic anhydride dissolves magnesia, forming the acetate $\text{MgAc}_2, 1.5\text{C}_2\text{H}_4\text{O}_2$, identical with the salt obtained by dissolving magnesium in acetic acid. One hundred parts of acetic acid dissolve 10 parts of the salt at 15°.

Calcium hydrogen acetate, $\text{CaAc}_2, \text{C}_2\text{H}_4\text{O}_2$, exists in two forms, (1) a voluminous, amorphous substance obtained by the slow action of a mixture of glacial acetic acid and acetic anhydride on chalk, or by the action of pure acetic acid on chalk crystallised by fusion in the electric furnace; (2) hard, transparent crystals obtained by dissolving chalk in boiling acetic acid, or by leaving the amorphous form in contact with acetic acid for several weeks. One hundred parts of acetic acid dissolve 6—7 parts of calcium acetate at 100°, and half the quantity at 20°.

Neither calcium nor magnesium acetate forms an acetochloride; magnesium acetate in acetic acid solution is partially converted into magnesium chloride by the prolonged action of chlorine, or more readily by the action of chlorine and water. M. A. W.

Some Double Salts of Lead. JOHN WHITE (*Amer. Chem. J.*, 1904, 31, 1—24).—The salt, $\text{PbI}(\text{C}_2\text{H}_3\text{O}_2), \text{NaC}_2\text{H}_3\text{O}_2, \frac{1}{2}\text{C}_2\text{H}_4\text{O}_2$, obtained by heating a mixture of sodium acetate and lead iodide with 80 per cent. alcohol containing a small proportion of acetic acid, crystallises in white, flat, orthorhombic plates; another salt, $\text{PbI}(\text{C}_2\text{H}_3\text{O}_2), 3\text{NaC}_2\text{H}_3\text{O}_2, \frac{1}{2}\text{C}_2\text{H}_4\text{O}_2$, is also produced and forms thin, pearly-white scales. The salt, $\text{PbI}(\text{C}_2\text{H}_3\text{O}_2), \text{KC}_2\text{H}_3\text{O}_2$, crystallises in pearly-white leaflets, and is probably identical with the compound obtained by Tommasi (*Abstr.*, 1872, 242), to which he assigned the

formula $2\text{PbI}(\text{C}_2\text{H}_3\text{O}_2), \text{KC}_2\text{H}_3\text{O}_2$. The salt, $\text{PbI}(\text{C}_2\text{H}_3\text{O}_2), \text{NH}_4 \cdot \text{C}_2\text{H}_3\text{O}_2$, crystallises in orthorhombic prisms; on evaporating the mother liquor, the double lead ammonium iodide described by Wells and Johnston (Abstr., 1893, 523) is obtained. The salt,

$\text{PbI}(\text{C}_2\text{H}_3\text{O}_2), \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2, \frac{1}{2}\text{C}_2\text{H}_4\text{O}_2$, forms well-defined, monoclinic prisms.

All these salts are almost instantaneously decomposed by water with formation of lead iodide and the basic iodide, $\text{PbI}(\text{OH})$. E. G.

Complex Zirconium Compounds. ALFRED MANDL (*Zeit. anorg. Chem.*, 1903, 37, 252—302).—Basic zirconium nitrate is an amorphous, white mass, easily soluble in water. Zirconium acetate is best prepared by adding ammonium acetate and dilute ammonia to a cold solution of zirconium nitrate, then dissolving the precipitate in acetic acid, and finally evaporating this solution. Zirconium carbonate is prepared by passing carbon dioxide through an aqueous solution of zirconium nitrate and ammonium carbonate.

Zirconium nitrate solution gives a precipitate with the potassium salts of many organic acids. In order to decide whether soluble double salts or complex salts were formed, a solution of zirconium nitrate was added to a definite volume of a solution of the potassium salt of the acid until no more precipitate formed. The precipitate with formic, acetic, and butyric acids respectively did not redissolve on the addition of excess of zirconium nitrate, whilst the precipitate with glycollic, lactic, and glyceric acids respectively did. In the last two cases, more zirconium solution was required than corresponded with one carboxyl group. A large number of other acids have been studied in this direction and the results are recorded.

Zirconium potassium oxalate, $\text{Zr}(\text{KC}_2\text{O}_4)_4, 5\text{H}_2\text{O}$, forms monoclinic prisms, easily soluble in water. Zirconium ammonium oxalate, $\text{Zr}(\text{NH}_4\text{C}_2\text{O}_4)_4, 6\text{H}_2\text{O}$, forms monoclinic crystals. Zirconium potassium malonate, $\text{Zr}(\text{CO}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{K})_4, 11\text{H}_2\text{O}$, is deliquescent and easily soluble in water. Zirconium potassium maleate,

$\text{Zr}(\text{CO}_2 \cdot \text{CH} \cdot \text{CH} \cdot \text{CO}_2\text{K})_4, \text{H}_2\text{O}$, is crystalline. Zirconium potassium glycollate, $\text{ZrK}_4(\text{C}_2\text{H}_3\text{O}_3)_8, 3\text{H}_2\text{O}$, separates from alcohol in microscopic prisms. Zirconium potassium malate, $\text{Zr}(\text{C}_4\text{H}_5\text{O}_5\text{K})_2, \text{C}_4\text{H}_6\text{O}_5, \text{C}_4\text{H}_5\text{KO}_5, 4\text{H}_2\text{O}$, is easily soluble in water. Zirconium potassium tartrate, crystals with $10\text{H}_2\text{O}$, and separates in monoclinic crystals. Zirconium potassium sodium tartrate forms microscopic prisms. Zirconium potassium citrate forms monoclinic needles and crystallises with $9\frac{1}{2}\text{H}_2\text{O}$.

The composition of zirconium hydroxide, dried over sulphuric acid at the ordinary temperature, is $\text{Zr}(\text{OH})_4$, whilst the hydroxide dried at 100° has the composition $\text{ZrO}(\text{OH})_2$.

Zirconium potassium β -resorcyate crystallises with $4\text{H}_2\text{O}$.

The condition for the formation of double salts and complex compounds is that the carboxylic acid in question must have two contiguous carboxyl groupings. Certain hydroxy-carboxylic acids with low dissociation constants are quoted; these either do not form double salts at all or yield double salts of highly complex structure.

A. McK.

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α -Iodopropionic Acid. WLADIMIR ZERNOFF (*Ber.*, 1903, 36, 4392—4394).—Propionic acid and phosphorus pentachloride are dissolved in chloroform and warmed to 65°, and iodine monochloride is added in small quantities until free iodine begins to separate. The mixture is poured into ice-water, and shaken first with sodium carbonate solution, then for several hours with water. The solution is dried, the chloroform removed, and the acid crystallised from light petroleum. It forms small prisms, melts at 44.5—45.5°, and is readily soluble in all organic solvents. The same acid may be obtained by hydrolysing the ester obtained by the action of potassium iodide on ethyl α -bromopropionate.

Most of the salts are readily soluble, the *lithium* salt contains H_2O ; the *magnesium* salt, $4\frac{1}{2}H_2O$; whilst the *copper* salt is anhydrous.
J. J. S.

Derivatives of Lauric Acid. GABRIEL GUÉRIN (*Bull. Soc. chim.*, 1903, [iii], 29, 1117—1124).—The lauric acid was prepared from a by-product obtained in refining cocoanut oil, and was separated from the associated fatty acids by fractional distillation of the mixed methyl esters under reduced pressure.

Methyl laurate melts at 5° and distils at 148° under 18 mm. pressure. *Lauroyl-o-toluidide*, $C_{11}H_{23}\cdot CO\cdot NH\cdot C_6H_4Me$, crystallises from ether and melts at 81—82°; the *p-toluidide* melts at 82—83°, and the *phenylhydrazide*, which forms brilliant spangles, melts at 105° and becomes yellow on exposure to air and light.

Lauroyl chloride condenses with tetrachloroquinol to form *dilauroyl-tetrachloroquinol*, which melts at 83—84°.

Octoic acid was obtained as a by-product in the preparation of lauric acid. Octoyl chloride condenses with tetrachloroquinol to form *dioctoyltetrachloroquinol*, which melts at 74°.
T. A. H.

Purification of Esters of High Molecular Weight by Vacuum Distillation. FRIEDRICH KRAFFT (*Ber.*, 1903, 36, 4339—4344).—The esters of the higher fatty acids give sharply-defined boiling points in the vacuum of the cathode light. The ethyl esters are comparatively volatile:

| | B. p. under 0 mm. (25 mm. column). | B. p. under 0 mm. (65 mm. column). |
|-----------------------|--|--|
| Ethyl stearate..... | 139° | 154° |
| Ethyl palmitate | 122 | 138 |
| Ethyl myristate | 102 | 121 |
| Ethyl laurate | 79 | 101 |

The ethylene esters, prepared by heating ethylene chloride with the dry potassium salts at 180°, crystallise from alcohol in colourless, glistening leaflets:

| | M. p. | B. p. under 0 mm. (20 mm. column). |
|----------------------------|-------|---------------------------------------|
| Ethylene distearate | 79° | 241° |
| Ethylene dipalmitate | 72 | 226 |
| Ethylene dimyristate | 64 | 208 |
| Ethylene dilaurate | 54 | 188 |

When the potassium salts are heated for 12—15 hours with an excess of ethylene chloride at 135°, or with ethylene bromide at 120—130°, the chloro- and bromo-ethyl esters are obtained :

| | M. p. | B. p. under 0 mm. |
|---------------------------------------|-------|----------------------|
| <i>β</i> -Chloroethyl palmitate | 44° | 138° |
| <i>β</i> -Bromoethyl palmitate | 62 | 144 |
| <i>β</i> -Chloroethyl myristate | 34 | 115 |
| <i>β</i> -Bromoethyl myristate | 48 | 134 |
| <i>β</i> -Chloroethyl laurate | 24 | 100 |
| <i>β</i> -Bromoethyl laurate | 36 | 124 |

These esters react with amines, forming *β*-amino-esters.

The monoglycerides, prepared by heating the potassium salts with *α*-monochlorohydrin in sealed tubes in an atmosphere of carbon dioxide, may be distilled in small vacuum vessels. These compounds have not been previously obtained in a state of purity :

| | M. p. | B. p. under 0 mm. |
|--|-------|----------------------|
| Monobenzoin, long crystals | 36° | 124° |
| Monolaurin, transparent, crystalline mass... | 59 | 142 |
| Monomyristin | 68 | 162 |
| Monopalmitin, crystallised from benzene ... | 72 | — |
| Monostearin, crystallised from benzene | 78 | — |
| Mono-olein, white crystals | 35 | — |

Benzoyl chloride and sodium hydroxide convert the monoglycerides into triglycerides. *Dibenzoylmonopalmitin*, $C_3H_5(OBz)_2 \cdot CO_2 \cdot C_{16}H_{31}$, melts at 69°, *dibenzoylmonomyristin*, $C_3H_5(OBz)_2 \cdot CO_2 \cdot C_{13}H_{27}$, crystallises from alcohol in white leaflets and melts at 65°.

The method may also be employed to isolate pure triglycerides from crude fats. In this way, pure trilaurin was obtained from laurel oil, and trimyristin from Japanese wax. Tripalmitin and stearin undergo slight decomposition when distilled, even under such low pressures.

C. H. D.

Nitric Esters of Hydroxy-acids. HENRI DUVAL (*Compt. rend.*, 1903, 137, 1262—1264).—*Glycolloglycollic acid nitrate*, $NO_2 \cdot O \cdot CH_2 \cdot CO \cdot O \cdot CH_2 \cdot CO_2H$, an amber-coloured oil, soluble in water, alcohol, or ether, slightly so in benzene, and insoluble in light petroleum, is formed as a secondary product in the nitration of glycollic acid (compare Abstr., 1903, i, 603, 676).

Lactic acid nitrate, $NO_2 \cdot O \cdot CHMe \cdot CO_2H$, is obtained by adding zinc lactate to a mixture of fuming nitric and concentrated sulphuric acids; after extracting with ether and drying for two weeks in a vacuum, the ester is obtained as a pale yellow oil, miscible with water, alcohol, ether, or benzene, and insoluble in ligroin.

α-Hydroxybutyric acid nitrate, $CH_2Me \cdot CH(O \cdot NO_2) \cdot CO_2H$, prepared similarly to the lactic acid nitrate, is a crystalline, colourless solid

melting at 45° and extremely soluble in water, alcohol, ether, or benzene, less so in light petroleum.

Methyl nitroglycollate, $\text{NO}_2 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$, is a colourless liquid with an agreeable colour, neutral to litmus, boiling with decomposition at 165° under the ordinary pressure and at 82.5° under 28 mm. pressure; it is soluble in alcohol, ether, or benzene, insoluble in water and light petroleum.

M. A. W.

α -Hydroxylauric Acid. GABRIEL GUÉRIN (*Bull. Soc. chim.*, 1903, [iii], 29, 1124—1128).— *α -Hydroxylauric acid*, prepared by brominating lauroyl chloride, treating the resulting product with water, and hydrolysing the α -bromolauric acid so formed with an aqueous solution of potassium hydroxide, is crystalline and melts at 73 — 74° . The sodium, potassium, copper, and lead salts were prepared; the ethyl ester melts at 43° .

α -Acetoxylauric acid melts at 47° , the ethyl ester is a liquid and boils at 172 — 173° under 13 mm. pressure.

α -Hydroxylauroylanilide melts at 83° and the *p*-toluidide at 100° .

T. A. H.

Stereoisomerism in the Esters of Substituted Camphocarboxylic Acids and Methylhomocamphoric Acid. Ethylcamphocarboxylic Acid. JULES MINGUIN (*Compt. rend.*, 1903, 137, 1067—1069).—When methylcamphocarboxylate is methylated, there is formed in addition to the solid α -methyl methylcamphocarboxylate, m. p. 85° , $[\alpha]_D + 17.25^{\circ}$ (Abstr., 1891, 1500), a liquid product from which the author has extracted a liquid stereoisomeride, *β -methyl methylcamphocarboxylate*, boiling between 135° and 140° under 13 mm. pressure, and having $[\alpha]_D + 75^{\circ}$. It is saponified by alcoholic potash in sealed tubes at 180° , yielding methylcamphor identical with that given by the α -compound under the same conditions (Abstr., 1892, 1343).

When methyl camphocarboxylate is treated with ethyl iodide and sodium methoxide, a liquid is obtained boiling at 167° under 10 mm. pressure; this is a mixture of the α - and β -stereoisomerides of methyl ethyl camphocarboxylate, the α -isomeride melts at 60° and has $[\alpha]_D + 58^{\circ}$; the β -compound is a liquid boiling at 162° under 10 mm. pressure and has $[\alpha]_D + 87.8^{\circ}$ (compare Brühl, Abstr., 1903, i, 6, 64; Haller, Abstr., 1903, i, 503). Each isomeride is saponified by alcoholic potash at 220° , forming ethylcamphor and small quantities of ethylcamphocarboxylic acid.

α -Methylhomocamphoric acid, $\text{CO}_2\text{H} \cdot \text{C}_8\text{H}_{14} \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$, m. p. 178 — 180° , $[\alpha]_D + 26.31^{\circ}$, has been prepared by the action of alcoholic potash on methylcyanocamphor (compare Haller and Minguin, Abstr., 1894, i, 338). The stereoisomeric β -derivative is obtained together with methylcamphor when methyl methylcamphocarboxylate is saponified in sealed tubes at 200° ; it melts at 143° and has $[\alpha]_D + 38.12^{\circ}$ (compare Rochussen, *Inaug. diss.*, 1897, Bonn; Brühl, Abstr., 1903, i, 6).

An attempt to prepare β -ethylhomocamphoric acid by saponifying methyl ethylcamphocarboxylate at 220° was unsuccessful; *ethylcampho-*

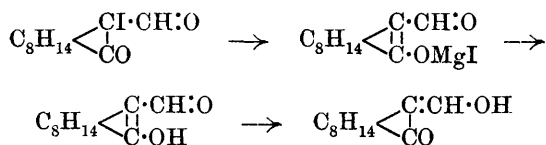
carboxylic acid, $C_8H_{14} \begin{smallmatrix} \diagup \\ \text{C} \cdot \text{CO}_2\text{H} \\ \diagdown \\ \text{CO} \end{smallmatrix}$, crystallising in needles, was the only product. M. A. W.

Camphocarboxylic Acid. VIII. JULIUS W. BRÜHL (*Ber.*, 1903, 36, 4272—4294. Compare *Abstr.*, 1903, i, 548).—The *benzoyl* derivative of *methylcamphocarboxylate*, $C_8H_{14} \begin{smallmatrix} \diagup \\ \text{C} \cdot \text{CO}_2\text{Me} \\ \diagdown \\ \text{C} \cdot \text{OBz} \end{smallmatrix}$, crystallises from alcohol in rhombic plates, melts at $58.5\text{--}59.5^\circ$, and gives, in alcoholic solution, no ferric chloride coloration. It is a benzoate and not a *C*-benzoyl derivative, since its saponification products are camphocarboxylic acid and benzoic acid.

When methyl bromocamphocarboxylate, $C_8H_{14} \begin{smallmatrix} \diagup \\ \text{C} \cdot \text{CO}_2\text{Me} \\ \diagdown \\ \text{CO} \end{smallmatrix}$, in ethereal solution is acted on by sodium, a yellowish-white residue is obtained, which on benzylation yields the benzoate. Enolisation had accordingly occurred during the action of sodium on the bromo-ester. The action of magnesium is partly analogous, although the magnesium does, to a slight extent, directly displace the bromine, attaching itself directly to carbon.

When methyl bromo-(or iodo)-camphocarboxylate is acetylated by magnesium and acetyl chloride according to Grignard's method, the presence of the *C*-acetyl derivative of methyl camphocarboxylate can be detected in the reaction product, and acetylcamphor was isolated as the product of its hydrolysis. The free bromocamphocarboxylic acid did not form a *C*-acetyl derivative when acted on by magnesium and ethyl acetate.

An ethereal solution of iodoformylcamphor was gradually added to magnesium, which was covered by dry ether, in an atmosphere of dry carbon dioxide. Hydroxymethylenecamphor was formed by the action of water on the product, thus:



When the reaction is accelerated, the carbon dioxide does, however, play a part, the compound $C_8H_{14} \begin{smallmatrix} \diagup \\ \text{C} \cdot \text{CH} \cdot \text{O} \\ \diagdown \\ \text{C} \cdot \text{O} \cdot \text{CO}_2\text{MgI} \end{smallmatrix}$ being probably formed.

When an ethereal solution of *oo*-dibromocamphor is acted on by magnesium in the presence of iodine and in an atmosphere of carbon dioxide, and the reaction product decomposed by water, camphocarboxylic acid is formed. *oo*-Di-iodocamphor behaves similarly.

Ethyl ethylacetoacetate can be extracted by ether from its aqueous solution in ice-cold 2 per cent. sodium hydroxide. Methyl camphocarboxylate behaves similarly. These two esters also resemble one

another in being more readily saponified by aqueous alkalis than is ethyl acetoacetate itself.

A *résumé* of the author's work on enolic derivatives of camphor is given. A. McK.

Splitting off of Hydrogen Ions from Methylene Groupings. JULIUS WAGNER and FELIX HILDEBRANDT (*Ber.*, 1903, 36, 4129—4131. Compare Vorländer, *Abstr.*, 1903, i, 230; Ehrenfeld, *Abstr.*, 1903, i, 548).—*N*/10 solutions of potassium tetroxalate, succinic acid, and citric acid respectively required the same amount of baryta for neutralisation. Such was also the case when *N*/50 solutions of potassium tetroxalate, tartaric, salicylic, and benzoic acids respectively were employed. Malonic acid, however, on titration in the cold with baryta, gave the same value as potassium tetroxalate, but the amount of baryta necessary for neutralisation diminished when the solution of malonic acid was heated, instead of increasing, as would be expected from Ehrenfeld's results. The authors surmise that malonic acid in a boiling aqueous solution undergoes slow decomposition into acetic and carbonic acids. A. McK.

Oxalates of Tervalent Thallium. W. OTTO RABE and HERMANN STEINMETZ (*Zeit. anorg. Chem.*, 1903, 37, 88—112. Compare *Abstr.*, 1902, ii, 491; 1903, i, 146).—A precipitate is formed when oxalic acid is added to a solution of a thallic salt, and in this respect thallium resembles scandium, yttrium, and lanthanum. Tervalent thallium tends to form acid oxalates, but not normal salts, and in this respect resembles aluminium, iron, and chromium.

Thallic oxalate, $\text{Th}_2(\text{C}_2\text{O}_4)_3$, prepared by adding an alcoholic solution of anhydrous oxalic acid to an alcoholic solution of thallic formate, was obtained as an amorphous precipitate. When oxalic acid is gradually added to thallic hydroxide, suspended in water, the *acid oxalate*, $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$, is obtained as a stable, white powder, which does not readily suffer hydrolytic dissociation, and which gives metallic thallium on being heated above 200° . It is instantly decomposed by aqueous alkalis. The *thallous thallic salt*, $\text{Th}_2(\text{C}_2\text{O}_4)_2 \cdot 3\text{H}_2\text{O}$, prepared by warming an aqueous solution of oxalic acid with thallic oxide, is soluble in water with difficulty, and from the solution thallic oxide is precipitated by the addition of alkali. When thallic hydroxide is allowed to remain at the ordinary temperature for several weeks with potassium hydrogen oxalate, a finely crystalline *potassium thallic oxalate*, $\text{KTh}(\text{C}_2\text{O}_4)_2 \cdot 3\text{H}_2\text{O}$, is formed. *Ammonium thallic oxalate*, $\text{NH}_4\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$, prepared in an analogous manner, parts with its water of crystallisation with difficulty. The *pyridine thallic oxalate*, $(\text{C}_5\text{NH}_6)\text{Th}(\text{C}_2\text{O}_4)_2$, was also prepared. When an excess of oxalic acid is added to a solution of thallic hydroxide in concentrated nitric acid, the *thallic hydrogen oxalate*, $\text{H}_4\text{Th}_2(\text{C}_2\text{O}_4)_5 \cdot 6\text{H}_2\text{O}$, is precipitated. The *pyridine thallic oxalate*, $(\text{C}_5\text{NH}_6)_3\text{Th}(\text{C}_2\text{O}_4)_3$, is also described (compare *Abstr.*, 1903, i, 146); by the action of ammonia on a concentrated ethereal solution of this compound, *ammonium thallic oxalate*, $(\text{NH}_4)_3\text{Th}(\text{C}_2\text{O}_4)_3$, is formed. When thallic oxalate is dissolved in a concentrated solution of potassium nitrite, a yellow, crystalline *salt* $\text{K}_8\text{Th}(\text{C}_2\text{O}_4)_2(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$, separates; it readily suffers hydrolytic disso-

ciation. The compound, $\text{NH}_4\text{Ti}(\text{C}_2\text{O}_4)_2 \cdot 2\text{NH}_3$, is prepared by passing ammonia into an alcoholic solution of thallic hydrogen oxalate at 0° . The compounds $\text{Ti}_2(\text{C}_2\text{O}_4)_3 \cdot 2\text{NH}_3$; $\text{KTi}(\text{C}_2\text{O}_4)_2 \cdot 2\text{NH}_3$; $(\text{C}_5\text{NH}_6)\text{Ti}(\text{C}_2\text{O}_4)_2 \cdot (\text{C}_5\text{NH}_5)_2$

are also described.

A. McK.

Electrolytic Synthesis of Glutaric Acid. L. VANZETTI and ANGELO COPPADORO (*Atti R. Accad. Lincei*, 1903, [v], 12, ii, 209—215).—Using as cathode solution, molecular proportions of ethyl succinate and malonate dissolved in water, and as anode liquid a 30 per cent. aqueous potassium carbonate solution, the authors obtain as products of electrolysis with platinum electrodes, the ethyl esters of succinic, glutaric, and adipic acids, together with a small proportion of an unsaturated ester (? ethyl acrylate). T. H. P.

Complete Synthesis of Camphoric Acid and Dehydrocamphoric Acid. GUSTAV KOMPPA (*Ber.*, 1903, 36, 4332—4335).—

On methylating methyl diketocamphorate, $\begin{array}{c} \text{CO} \cdot \text{CH}(\text{CO}_2\text{Me}) \\ \text{CO} \cdot \text{CH}(\text{CO}_2\text{Me}) \end{array} > \text{CMe}_2$ (Abstr., 1901, i, 668), with sodium (1 atom) and methyl iodide, an oil is obtained from which aqueous sodium carbonate extracts principally

methyl diketocamphorate, $\begin{array}{c} \text{CO} \cdot \text{CH}(\text{CO}_2\text{Me}) \\ \text{CO} \cdot \text{CMe}(\text{CO}_2\text{Me}) \end{array} > \text{CMe}_2$, the copper salt of which, $\text{C}_{24}\text{H}_{30}\text{O}_{12}\text{Cu}$, is soluble in ether and thus renders purification easy. The ester, $\text{C}_{12}\text{H}_{16}\text{O}_6$, liberated from the copper salt, crystallises from methyl alcohol in beautiful, thick, apparently monoclinic plates, melts at $85\text{--}88^\circ$, and on reduction with sodium amalgam gives

dihydroxycamphoric acid, $\begin{array}{c} \text{OH} \cdot \text{CH} \cdot \text{CH}(\text{CO}_2\text{H}) \\ \text{OH} \cdot \text{CH} \cdot \text{CH}(\text{CO}_2\text{H}) \end{array} > \text{CMe}_2$, in the form of a syrup; the barium and silver salts were analysed. On reducing this acid with hydriodic acid of sp. gr. 1.7, a crystalline, racemic de-

hydrocamphoric acid, $\begin{array}{c} \text{CH}=\text{C}(\text{CO}_2\text{H}) \\ \text{CH}_2 \cdot \text{CMe}(\text{CO}_2\text{H}) \end{array} > \text{CMe}_2$ or $\begin{array}{c} \text{CH} \cdot \text{CH}(\text{CO}_2\text{H}) \\ \text{CH} \cdot \text{CMe}(\text{CO}_2\text{H}) \end{array} > \text{CMe}_2$,

is obtained, which crystallises from very dilute alcohol in stellate aggregates of microscopic prisms, melts at $221\text{--}223^\circ$, and combines with hydrogen bromide in glacial acetic acid solution at $120\text{--}125^\circ$ to

form a β -bromocamphoric acid, $\begin{array}{c} \text{CHBr} \cdot \text{CH}(\text{CO}_2\text{H}) \\ \text{CH}_2 \cdot \text{CMe}(\text{CO}_2\text{H}) \end{array} > \text{CMe}_2$ (?). This, on reduction with zinc dust and acetic acid, gives racemic camphoric acid identical in every respect with Chautard's substance.

The compound $\begin{array}{c} \text{OMe} \cdot \text{C}=\text{C}(\text{CO}_2\text{Me}) \\ \text{CO} \cdot \text{CMe}(\text{CO}_2\text{Me}) \end{array} > \text{CMe}_2$ is formed simultaneously with methyl diketocamphorate in the original methylation; it is a colourless liquid which boils at $167\text{--}168^\circ$ under 12 mm. pressure, and on reduction with sodium amalgam gives the dihydroxycamphoric acid already described. W. A. D.

Chemico-Physical Properties of the Malates of the Alkaline Earths. LUDOVICO CANTONI and VERATIETTI (*Gazzetta*, 1903, 33, ii, 139—145).—The authors have made a number of experiments on the separation of barium, calcium, and strontium malates from solutions in presence of ammonia. Three principal factors are found to come into play, namely, the concentration, temperature, and nature of the solution. The method of preparation employed is expressed by the equation: $MCl_2 + C_4H_6O_5 + 2NH_3 = 2NH_4Cl + C_4H_4O_5M$; M being the alkaline earth metal. The results obtained are tabulated.

T. H. P.

Derivatives of Comenic Acid. A. TAMBURELLO (*Gazzetta*, 1903, 33, 264—266).—When concentrated ammonia is added to ethyl comenate, it dissolves, and, on adding silver nitrate, a comparatively stable silver salt is precipitated, which can be washed without decomposing; on agitating this salt with cold alcoholic ethyl iodide, *ethyl comenamide*, $OEt \cdot C_5H_2O_2 \cdot CO \cdot NH_2$, is obtained, which separates from alcohol in white, lustrous crystals and melts at 159—160°.

The following compounds were obtained from the ordinary silver salt of ethyl comenate (Oliveri, Abstr., 1900, i, 587) by the action of alkyl iodides.

Ethyl comenate amyl ether, $C_5H_{11}O \cdot C_5H_2O_2 \cdot CO_2Et$, crystallises from alcohol in large, hard, white prisms and melts at 79—80°. *Ethyl comenate isopropyl ether* crystallises in minute, white needles and melts at 123°.

W. A. D.

Undecaldehyde. EDMOND E. BLAISE and GABRIEL GUÉRIN (*Bull. Soc. chim.*, 1903, [iii], 29, 1202—1208).—*Undecaldehyde*, $C_{10}H_{21} \cdot CHO$, was prepared from hydroxylauric acid by a slight modification of Baeyer's method (Abstr., 1897, i, 588). It is crystalline, has a characteristic, persistent odour, melts at -4° , and polymerises spontaneously, but more rapidly on addition of a few drops of sulphuric acid. The *polymeride*, $(C_{11}H_{22}O)_3$, is odourless, crystallises in needles or lamellæ, melts at 47—48°, has n_D 1.4322 at 23° and a sp. gr. 0.8251 at 23°/4°. The aldehyde gives all the usual colour reactions of the aliphatic aldehydes, does not combine with sodium hydrogen sulphite, being polymerised by this reagent, and condenses with β -naphthylamine and pyruvic acid (compare Doebner, Abstr., 1894, 261) to form *2-decyl- β -naphthucinchoninic acid*, which can be crystallised from methyl alcohol. With semicarbazide hydrochloride, undecaldehyde furnishes a *semicarbazone*, which is crystalline and melts at 103°; the *oxime* crystallises from methyl alcohol in white needles and melts at 72°.

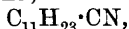
Diundecylideneazine, $N_2 \cdot (CH \cdot C_{10}H_{21})_2$, obtained by condensing the aldehyde with hydrazine, melts at 57° and is very soluble in light petroleum. Undecaldehyde, when reduced by Kraft's method (Abstr., 1883, 1075), gives *undecyl alcohol*, which has a pleasant odour, boils at 146° under 30 mm. pressure, melts at 11°, has a sp. gr. 0.8334 at 23°/4° and n_D 1.4392 at 23°, and a crystalline condensation product of the alcohol, having the composition $C_{22}H_{46}O$.

T. A. H.

Methyl Undecyl Ketone. GABRIEL GUÉRIN (*Bull. Soc. chim.*, 1903, [iii], 29, 1128—1131).—When ethyl sodioacetoacetate is treated with lauryl chloride and the resulting mixture of *O*- and *C*-esters is hydrolysed by an aqueous solution of potassium hydroxide, methyl undecyl ketone is formed from the *C*-ester (compare Bouveault and Bongert, *Abstr.*, 1901, i, 311).

The *oxime* crystallises from ether on addition of light petroleum, is very soluble in alcohol and chloroform, less so in ether, and almost insoluble in benzene, and melts at 56—57°. The *semicarbazone* crystallises from boiling methyl alcohol and melts at 123°. T. A. H.

Ethyl Undecyl Ketone. EDMOND E. BLAISE and GABRIEL GUÉRIN (*Bull. Soc. chim.*, 1903, [iii], 29, 1208—1211).—*Lauroitrile*,



obtained by dehydrating lauramide with phosphoric oxide, has a characteristic, persistent odour, melts at 4°, and distils at 198° under 100 mm. pressure. When treated with metallic magnesium and ethyl iodide by the general method already described (*Abstr.*, 1902, i, 164), it furnishes *ethyl undecyl ketone*, $\text{C}_{11}\text{H}_{23}\cdot\text{COEt}$. This is crystalline, melts at 34°, and distils at 152° under 16 mm. pressure; its *oxime* melts at 40°, and the *semicarbazone* at 92°. Both these derivatives crystallise well from methyl alcohol. T. A. H.

Action of Phosphorus Pentachloride on Methyl Undecyl Ketoxime. EDMOND E. BLAISE and GABRIEL GUÉRIN (*Bull. Soc. chim.*, 1903, [iii], 29, 1211—1216. Compare preceding abstracts).—When methyl undecyl ketoxime, $\text{C}_{11}\text{H}_{23}\cdot\text{CMe}\cdot\text{NOH}$, dissolved in ether, is treated with phosphorus pentachloride, but little action occurs unless the latter is present in large excess and the mixture is boiled. In these circumstances, *acetylundecylamide*, $\text{C}_{11}\text{H}_{23}\cdot\text{NHAc}$ (which forms minute needles, melting at 47—48°), is the only amide produced, and on hydrolysis furnishes undecylamine and acetic acid. This result indicates that undecyl methyl ketoxime is homogeneous and not a mixture of stereoisomerides.

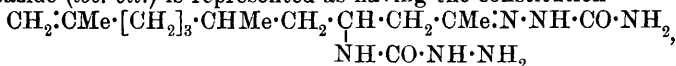
The authors suggest that the different behaviour of aliphatic ketoximes towards phosphorus pentachloride may be explained by assuming that in this reaction there is a tendency to form the amide of the more energetic acid, that is, the one having the alkyl group of less mass. Where the two alkyl groups of the ketoxime are not very dissimilar in mass, two amides are formed, but in different proportions. This suggestion is in accordance (*a*) with the formation of undecylacetamide from methyl undecyl ketoxime, (*b*) with Hantzsch's observation that all ketoximes having methyl as one alkyl group furnish a substituted acetamide, and (*c*) with the observation that from methyl ethyl ketoxime 66 per cent. of ethylacetamide and 33 per cent. of methylpropionamide are obtained (*Hantzsch, Abstr.*, 1892, 426).

A similar rule probably also governs the hydrolytic decompositions of the acylacetoacetic esters studied by Bouveault and Bongert (*Abstr.*, 1901, i, 311; 1903, i, 63, 141, and 142).

In the case of transformation of the oximes, however, some influence

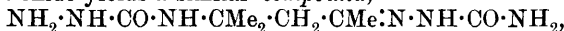
appears to be exerted also by the reagent employed (compare Houben, Abstr., 1903, i, 47). T. A. H.

Action of Semicarbazide on Unsaturated Ketones. HANS RUPE and PAUL SCHLOCHOFF (*Ber.*, 1903, 36, 4377—4384. Compare Rupe and Lotz, Abstr., 1903, i, 841).—The compound obtained by the condensation of citronellideneacetone with two molecules of semicarbazide (*loc. cit.*) is represented as having the constitution



and is termed *citronellideneacetonesemicarbazidesemicarbazone*.

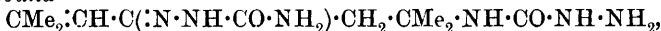
Mesityl oxide yields a similar compound,



which crystallises in small, colourless plates, melting at 220°, and dissolves in dilute hydrochloric acid, but is practically insoluble in the ordinary organic solvents. When boiled with water, an odour of mesityl oxide is noticed, and hydrazidocarbonamide (Thiele, Abstr., 1892, 1298, 1429) and Scholtz's (Abstr., 1896, i, 343) and Harries' (Abstr., 1899, i, 637) compound melting at 129° are obtained.

Acetic anhydride converts the compound into acetylsemicarbazide, and nitrous acid yields a *nitrosoamine* melting at 146°. Benzylideneacetone, cinnamoylacetone, and pulegone yield the ordinary semicarbazones, which do not react with a second molecule of semicarbazide. This is probably due to the presence of the phenyl radicle.

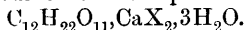
Phorone also reacts with semicarbazide (2 mols.), yielding the compound



which may be crystallised from hot water; it melts at 221°, is hydrolysed by hydrochloric acid, and shows no tendency to undergo ring formation (Harries, Abstr., 1897, i, 211). When treated with sodium nitrite and hydrochloric acid, it yields a *nitroso-derivative* melting at 140°, together with a second compound melting at 169°.

J. J. S.

Compounds of Sucrose with Metallic Salts. D. GAUTHIER (*Compt. rend.*, 1903, 137, 1259—1260).—The author has prepared a number of crystalline compounds of sucrose and the halogen salts of the alkali metals and of the metals of the alkaline earths. The compound with potassium iodide, $\text{C}_{12}\text{H}_{22}\text{O}_{11}\cdot\text{KI}\cdot 2\text{H}_2\text{O}$, forms crystals several centimetres in length. The compounds with the three lithium haloids have the general formula $\text{C}_{12}\text{H}_{22}\text{O}_{11}\cdot\text{LiX}\cdot 2\text{H}_2\text{O}$. Calcium bromide and iodide form compounds of the type



The sucrose compounds with strontium chloride and bromide are crystalline, but take a long time to form, whilst the three barium haloids yield voluminous crystalline compounds which are anhydrous and have the general formula $2\text{C}_{12}\text{H}_{22}\text{O}_{11}\cdot\text{BaX}_2$. M. A. W.

Nitrocelluloses. CARL HAEUSSERMANN (*Ber.*, 1903, 36, 3956).—When collodion cotton, gun-cotton, or nitrated sulphite-cellulose is distilled with aqueous sodium hydroxide or with baryta, strontia, or

lime water, a small quantity of a *substance* passes over which gives the ordinary reactions of an aldehyde. W. A. D.

Composition of Silver Compounds of Methylamine and Ethylamine existing in Solution. GUIDO BODLÄNDER and W. EBERLEIN (*Ber.*, 1903, 36, 3945—3951. Compare Bodländer and Fittig, *Abstr.*, 1902, ii, 248).—Wuth's measurements (*Abstr.*, 1902, i, 594) of the solubility of silver chloride and bromide in methylamine and ethylamine are incorrect throughout; the values obtained by the authors show that the product of the amount of dissolved silver haloid by its dissociation is proportional to the concentration of the free base and not to the fourth root of this. If the formula of the complex salt be $\text{Ag}_m\text{B}_n\text{Cl}_m$, that of the complex iron is Ag_mB_n , and the formula of decomposition into free base and silver ions becomes $\text{Ag}^m\text{B}^n = k_1 D$, D denoting the amount of dissolved silver chloride. The concentration of the silver ions is determined by that of the chlorine ions according to the equation $\text{Ag}^m D^m = k_2^m$, where $k_2 = [\text{Ag}][\text{Cl}]$; whence $\text{B}^n = (k_1/k_2^m) \cdot D^{m+1}$. But experimentally B/D was found constant, and this is reconcilable with formula (i), when $m = 1$, $n = 2$, or $m = 2$, $n = 3$, and so on. The formula of the complex salt must therefore be AgB_2Cl , $\text{Ag}_2\text{B}_3\text{Cl}_3$, $\text{Ag}_3\text{B}_4\text{Cl}_3$, &c., and Wuth's formula, Ag_3BCl_3 , is excluded.

By measuring the *E.M.F.* of concentration cells containing the same quantity of base with different amounts of silver nitrate and chloride, using the formula $E = 0.058/m \cdot \log D_1/D_2$, the value of m was found to be approximately unity; similarly, from the *E.M.F.* of cells containing different quantities of the base, using the formula $E = n/m \cdot 0.058 \cdot \log B_2/B_1$, n was ascertained to be nearly 2. The formulæ of the complexes are therefore $\text{Ag}(\text{NH}_2\text{Me})_2\text{X}$, and $\text{Ag}(\text{NH}_2\text{Et})_2\text{X}$. W. A. D.

Synthesis of Betaines from Dialkylated Aminonitriles. AUGUST KLAGES and S. MARGOLINSKY (*Ber.*, 1903, 36, 4188—4194).—The methiodide of diethylaminoacetonitrile melts at 190—195° instead of at 205° (*Abstr.*, 1902, i, 354); by moist silver oxide, it is hydrolysed to methyl-diethylbetainenitrile, the *picrate* of which melts at 166—168°. The ethiodide, after repeated recrystallisation, melts at 184°. Triethylbetainenitrile forms a *picrate* crystallising from water in glistening needles melting at 193°, an *aurichloride* melting at 118—119°, and a *mercurichloride* melting at 130—131°.

The *methiodide* of α -diethylaminopropiononitrile melts at 195—196° and, when hydrolysed, forms *methyl-diethylpropionobetaine*, which melts at 117—119° and gives an *aurichloride* melting at 200—202°. The *ethiodide* of this nitrile melts and decomposes at 178—179°; *triethylpropionobetaine* melts at 90—92°, and its *aurichloride* at 253°.

Diethylaminophenylacetoneitrile, $\text{NEt}_2 \cdot \text{CHPh} \cdot \text{CN}$, is a faintly yellow oil boiling at 142° under 16 mm. pressure, and having a sp. gr. 0.9736 at 19°/4°. It was not found possible to hydrolyse this to the corresponding acid, either the *amide*, which crystallises in colourless crystals melting at 142—143°, or mandelic acid and diethylamine being formed. The *methiodide* forms colourless needles melting at 128—129°;

α -phenylmethyldiethylbetaine, $\text{NMeEt}_2\text{CHPhCO}$, separates as a white, hygroscopic powder.

Piperidoacetoneitrile is a colourless oil boiling at $99\text{--}100^\circ$ under 15 mm. pressure, which crystallises in glistening crystals melting at 19° , and has a sp. gr. 0.9678 at $14^\circ/4^\circ$; the *methiodide* separates in colourless plates melting at $192\text{--}193^\circ$, and the corresponding *methylpiperidobetaine* is a colourless, hygroscopic powder, which melts at $116\text{--}118^\circ$ and yields an *aurichloride* melting at $178\text{--}179^\circ$.

E. F. A.

Action of Amyl Nitrite on Ethyl β -Aminocrotonate. HANS EULER and ASTRID EULER (*Ber.*, 1903, 36, 4246—4253).—The ammonium derivative of ethyl γ -isonitroso- β -nitrosoaminocrotonate, $\text{NH}_4\cdot\text{O}\cdot\text{N}:\text{CH}\cdot\text{C}(\text{NH}\cdot\text{NO})\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, prepared by the action of amyl nitrite on ethyl β -aminocrotonate dissolved in ether, crystallises in colourless, glistening scales and melts and decomposes at 170° ; the monopotassium derivative, $\text{C}_6\text{H}_8\text{O}_4\text{N}_3\text{K}\cdot\text{H}_2\text{O}$, prepared by oxidising the ammonium derivative with potassium permanganate, forms minute, glistening, colourless needles and explodes at 233° ; the dipotassium derivative, $\text{C}_6\text{H}_7\text{O}_4\text{N}_3\text{K}_2$, forms colourless needles and melts at 232° ; the dibarium derivative, $\text{C}_6\text{H}_7\text{O}_4\text{N}_3\text{Ba}$, forms a heavy, insoluble, brown powder; the monozinc derivative, $(\text{C}_6\text{H}_8\text{N}_3\text{O}_4)_2\text{Zn}$, is sparingly soluble in hot water, insoluble in alcohol.

Ethyl γ -isonitrosoacetoacetate, $\text{OH}\cdot\text{N}:\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, prepared by the action of nitrous acid on the ammonium derivative just described, forms transparent, volatile tablets and melts at about 50° .

A compound, $\text{C}_6\text{H}_8\text{O}_4\text{N}_2$, probably $\text{N}\begin{smallmatrix} \text{CH}\cdot\text{C}\cdot\text{CH}\cdot\text{CO}_2\text{Et} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{N}\cdot\text{OH} \end{smallmatrix}$, prepared by the action of hydrobromic acid on the ammonium derivative, forms colourless needles and melts without decomposition at 90° .

T. M. L.

Action of Amyl Nitrite on Ethyl β -Aminocrotonate. HANS EULER and ASTRID EULER (*Ber.*, 1903, 36, 4366).—The compounds $\text{C}_6\text{H}_{12}\text{O}_4\text{N}_4$, melting at 170° , and $\text{C}_6\text{H}_{10}\text{O}_4\text{N}_2$, melting at $89\text{--}90^\circ$, prepared by the interaction of amyl nitrite and ethyl β -aminocrotonate, have already been obtained by W. Strecker (*Dissertation Heidelberg*, 1900).

E. F. A.

Copper Thiocyanocyanides. HERMANN GROSSMANN (*Zeit. anorg. Chem.*, 1903, 37, 407—410).—The clear solution, obtained by dissolving mercuric chloride (1 mol.) and potassium thiocyanate (4 mols.) in water, contains potassium mercuric tetrathiocyanate, $\text{K}_2\text{Hg}(\text{CNS})_4$, and potassium chloride; the addition of potassium cyanide (2 mols.) causes the precipitation of the salt $\text{CuCN}\cdot 2\text{KCN}\cdot \text{KCN}\cdot \frac{1}{2}\text{H}_2\text{O}$ in brilliant, glistening needles. The salt $2\text{CuCN}\cdot 3\text{KCN}$, prepared from cuprous cyanide and potassium thiocyanate, forms rhombic plates. The salt $2\text{CuCN}\cdot 3\text{NH}_4\text{CNS}$ also crystallises in rhombic plates.

Cuprous cyanide is soluble with difficulty in concentrated solutions of alkali haloids.

A. McK.

Halogen Thiocyanates. Relationships between the Rhodanic, Halogen, and Cyanogen Ions. HERMANN GROSSMANN (*Zeit. anorg. Chem.*, 1903, 37, 411—447).—Whilst mercuric thiocyanate is precipitated from a solution of mercuric nitrate and potassium thiocyanate, there is no precipitation when mercuric chloride is used, since the tendency of the nitrate to form complexes with the potassium salts present is less than that of the chloride. *Cadmium mercuric thiocyanate*, $\text{CdHg}(\text{CNS})_4$, separates from water in tetragonal plates. Mercuric thiocyanate is readily soluble in hot concentrated solutions of potassium and ammonium chlorides respectively, and, on cooling, the salts $\text{Hg}(\text{CNS})_2, \text{NH}_4\text{Cl}$ and $\text{Hg}(\text{CNS})_2, \text{KCl}$ respectively separate. Both are decomposed by water with the regeneration of mercuric thiocyanate. A mixture of complex salts is formed when mercuric thiocyanate is dissolved in a concentrated solution of potassium bromide. When, however, mercuric thiocyanate (1 mol.) is dissolved in an aqueous solution of potassium bromide (2 mols.), the salt $\text{Hg}(\text{CNS})_2, 2\text{KBr}$, crystallising in needles, is produced. The ammonium salt, $\text{Hg}(\text{CNS})_2, \text{NH}_4\text{Br}$, was also prepared.

The salt $\text{KCNS}, \text{HgBr}_2$ separates from an alcoholic solution of its components. When mercuric bromide is dissolved in concentrated barium thiocyanate solution, the salt $\text{Ba}(\text{CNS})_2, 2\text{HgBr}_2, 5\text{H}_2\text{O}$ separates in glistening needles. The salt $2\text{KCNS}, \text{HgI}_2$ does not contain water of crystallisation. The salt $2\text{NH}_4\text{CNS}, \text{HgI}_2$ is also anhydrous. The following compounds were also prepared: $\text{Cd}(\text{CNS})_2, 2\text{KCl}$; $\text{Cd}(\text{CNS})_2, 2\text{NH}_4\text{Cl}$; $\text{Cd}(\text{CNS})_2, \text{NH}_4\text{Br}, \text{H}_2\text{O}$; $\text{Cd}(\text{CNS})_2, \text{KBr}, \text{H}_2\text{O}$; $\text{Cd}(\text{CNS})_2, 2\text{KBr}$; $\text{Cd}(\text{CNS})_2, 2\text{NH}_4\text{Br}$; $2\text{NH}_4\text{CNS}, \text{CdI}_2$, and $2\text{KCNS}, \text{CdI}_2$.

The substances described can be formulated according to Werner's system.

The tendency of the rhodanic ion to form complex ions is discussed.

The relationship of complex haloid salts to complex thiocyanates is close. A systematic classification of all the known complex thiocyanates is appended.

A. McK.

Relative Stability of Carbonylferrocyanides towards Oxidising Agents. JOSEPH A. MULLER (*Bull. Soc. chim.*, 1903, [ii], 29, 1158—1161. Compare Abstr., 1903, i, 238).—The author finds that potassium carbonylferrocyanide is much more stable towards oxidising agents than is potassium ferrocyanide; it is, for example, not attacked by potassium persulphate, and only slightly so by potassium permanganate or ozone in the absence of sulphuric acid. Similarly, nitric acid, at atmospheric temperature, produces little effect. In the presence of sulphuric acid, ozone liberates a small quantity of hydrogen cyanide, and potassium permanganate is rapidly decolorised, hydrogen cyanide being evolved even in the cold, and more rapidly as the temperature is raised to 40—50°.

T. A. H.

Carbonylferrocyanides. JOSEPH A. MULLER (*Bull. Soc. chim.*, 1903, [iii], 29, 1161—1166. Compare Abstr., 1903, i, 238, and preceding abstract).—When a solution of potassium carbonylferrocyanide is vigorously agitated during 40 seconds in an atmosphere of chlorine, approximately one atom of chlorine is absorbed (apart from that

mechanically dissolved by the solution) by each molecule of the carbonylferrocyanide present. The resulting liquid is precipitated by solutions of copper salts, furnishing a *product* having the composition represented by the formula $\text{Cu}_6\text{KFe}_5(\text{CO})_5(\text{CN})_{25}$. This is a dark green, hygroscopic powder, in which the relation of "ferric" to "ferrous" iron is as 2:3, and which, when treated with an aqueous solution of sodium hydroxide, gives an intensely yellow liquid, which in presence of dilute sulphuric acid gives a blue coloration with a solution of potassium iodide in starch mucilage, a violet-blue precipitate with ferric chloride, a blue precipitate with ferrous chloride, a brownish-apple-green precipitate with copper acetate, and a brownish-lilac precipitate with cobalt nitrate. The alkaline liquid is unstable, decomposing slowly at atmospheric temperatures and more rapidly on warming, with the deposition of a precipitate containing ferric oxide, and the formation in solution of sodium ferrocyanide (1 part) and carbonylferrocyanide (3 parts).

It is probable that the first result of the action of chlorine on the potassium carbonylferrocyanide is the formation of potassium chloro-carbonylferrocyanide, $\text{K}_3\text{FeClCO}(\text{CN})_5$, which, on addition of a soluble copper salt, is converted into the green salt already described, part of the chlorine forming potassium chloride and the rest being evolved in the free state.

When the action of chlorine on potassium carbonylferrocyanide is prolonged, carbon dioxide is evolved, and a considerable quantity of potassium ferricyanide is formed. This decomposition is accelerated by the presence of potassium carbonate. Hydrogen peroxide appears to react with potassium carbonylferrocyanide at 60° in a manner similar to chlorine.

T. A. H.

Derivatives of α -Aminopropionitrile. MARCEL DELÉPINE (*Bull. Soc. chim.*, 1903, [iii], 29, 1190—1196).— α -Aminopropionitrile is monobasic to methyl-orange, does not react with phenolphthalein, and behaves in an indefinite manner with litmus: the hydrochloride, *sulphate*, platinichloride, *picrate*, and *tartrate* were prepared, and are described. When α -aminopropionitrile *sulphate*, dissolved in water, is boiled with a slight excess of barium hydroxide for 5 or 6 hours, it is converted into alanine, without the formation of the coloured by-products obtained when the hydrolysis is effected with hydrochloric acid. Iminopropionitrile is similarly converted by barium hydroxide into the corresponding acid.

α -Acetylaminopropionitrile, $\text{CN}\cdot\text{CHMe}\cdot\text{NHAc}$, obtained by warming the nitrile, dissolved in benzene, with acetic anhydride, crystallises from alcohol in rectangular lamellæ, melts at 102° , and is soluble in water and ether. The corresponding *benzoyl* derivative crystallises in plates, melts at 108° , and is very soluble in alcohol, soluble in water, and less so in ether. *l*-Benzoylaminopropionitrile crystallises in brilliant needles, melts at $123\cdot5^\circ$, has $[\alpha]_D -55\cdot84^\circ$ at 15° in alcohol, and on hydrolysis with barium hydroxide furnishes *r*-benzoylamino-propionic acid: the *dextro*-isomeride melts at 115 — 120° and has $[\alpha]_D +41\cdot3^\circ$ under the same conditions.

When α -aminopropionitrile, dissolved in ether, is treated with

phenylcarbimide, there is formed *phenyl- α -cyanoethylcarbamide*,
 $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CN}$,

which is crystalline, melts at 135° , and is converted by warming with alcohol and hydrochloric acid into α -phenyl- δ -methylhydantoin (Mouneyrat, Abstr., 1900, i, 644).

With methylthiocarbimide, α -aminopropionitrile gives a viscous product, which on hydrolysis furnishes $\alpha\delta$ -dimethylthiohydantoin (Abstr., 1896, i, 149). Similarly, it condenses with phenylthiocarbimide to form *phenyl- α -cyanoethylthiocarbamide* (minute crystals), which is hydrolysed by hydrochloric acid to α -phenyl- δ -methylthiohydantoin (*loc. cit.*).

When α -aminopropionitrile *d*-tartrate, which crystallises in colourless needles containing $2\text{H}_2\text{O}$ and has $[\alpha]_D + 17.3^\circ$, is dissolved in three times its weight of water and there is added to the solution an equal volume of alcohol, a precipitate having $[\alpha]_D + 12.6^\circ$ is obtained; by the addition of ether to the mother liquor, a precipitate having $[\alpha]_D + 18^\circ$ is separated, and finally, by evaporation of the filtrate, a residue having $[\alpha]_D + 23^\circ$ is procured. The extreme fractions are the *d*-tartrates of *l*- and *d*- α -aminopropionitrile respectively. Both salts contain H_2O ; the solubility of that of the *d*-base in 80 per cent. alcohol is 1.91 grams per 100 c.c., and that of the *l*-base in the same solvent 0.66 grams per 100 c.c.; the sulphate of the *l*-base has $[\alpha]_D - 11.4^\circ$, and that of the *d*-base $[\alpha]_D + 10^\circ$.
T. A. H.

Basicity of α -Aminonitriles. MARCEL DELÉPINE (*Bull. Soc. chim.*, 1903, [iii], 29, 1196—1198. Compare preceding abstract).—The author finds that the heat of neutralisation of aminoacetonitrile (Klages, Abstr., 1903, i, 469) by sulphuric acid is 19.86 Cal. at 21° and that of α -aminopropionitrile 20.55 Cal. at 14° , those of the corresponding amines, methylamine and ethylamine, being respectively 30.1 and 30.4 Cal. In both cases, the ethyl compound has the higher heat of neutralisation. The introduction of a cyanogen group in the α -position appears to reduce the heat of neutralisation of the parent amine by about 10 Cal. The salts of the two α -aminonitriles appear to undergo comparatively little dissociation on solution in water, since the values of the heats of neutralisation are but little affected by the state of dilution of the salt produced.
T. A. H.

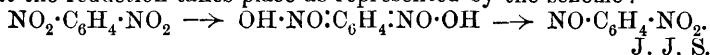
Unsaturated Acids of the Sorbic Series and their Transformation into Cyclic Hydrocarbons. OSCAR DOEBNER and H. STAUDINGER (*Ber.*, 1903, 36, 4318—4326. Compare Abstr., 1902, i, 598).—Both cinnamylacrylic and allocinnamylacrylic acids give the same substances when distilled with anhydrous barium hydroxide; these consist of the saturated hydrocarbons phenylcyclobutadiene, $\text{CHPh}\langle\begin{smallmatrix}\text{CH} \\ | \\ \text{CH}\end{smallmatrix}\rangle\text{CH}_2$ or $\text{CHPh}\langle\begin{smallmatrix}\text{CH} \\ | \\ \text{CH}_2\end{smallmatrix}\rangle\text{CH}$, and diphenylcyclooctadiene, which have already been described (*loc. cit.*), a phenylbutylene which boils at 73° under 18 mm. pressure, probably identical with the "phenylbutene" of Harries and de Osa (Abstr., 1903, i, 815), and an isocyclobutadiene, $(\text{C}_{10}\text{H}_{10})_x$, formed in very small quantity, which melts at $100\text{--}101^\circ$ and boils at $155\text{--}165^\circ$ under 16 mm. pressure.

On distillation with quinoline, the same acids give rise only to unsaturated hydrocarbons, namely, phenylbutadiene and diphenyldibutadiene (bisphenylbutadiene, Liebermann and Riiber, *Abstr.*, 1902, i, 669).

W. A. D.

Reduction of Dinitrobenzenes. JAKOB MEISENHEIMER (*Ber.*, 1903, 36, 4174—4177).—When a solution of *o*-dinitrobenzene in methyl-alcoholic potash is reduced with hydroxylamine, also dissolved in methyl alcohol, the liquid turns a deep bluish-violet colour, oxygen is evolved, and on the addition of dilute hydrochloric acid *o*-nitro-nitrosobenzene is obtained (compare Bamberger and Hübner, this vol., i, 115).

When *p*-dinitrobenzene is reduced in a similar manner, a yellow *potassium* salt, $\text{OK} \cdot \text{NO} \cdot \text{C}_6\text{H}_4 \cdot \text{NO} \cdot \text{OK}$, is obtained. It is soluble in water, but the solution decomposes when heated, and when acidified yields *p*-nitronitrosobenzene melting at 118—119°. It is probable that the reduction takes place as represented by the scheme:



J. J. S.

A New Chlorotrinitrobenzene. RUDOLF NIETZKI and WALDEMAR ZÄNKER (*Ber.*, 1903, 36, 3953—3955).—When 1-chloro-3:4-dinitrobenzene dissolved in 40 per cent. pyrosulphuric acid is added to a mixture of sulphuric monohydrate and nitric acid of sp. gr. 1.52, 1-chloro-3:4:6-trinitrobenzene is obtained, which crystallises from alcohol in yellow leaflets and melts at 116°; when gently warmed with ammonia, 1-chloro-4:6-dinitro-3-aminobenzene is formed. The displacement of the chlorine atom needs a higher temperature.

W. A. D.

Substituted Benzhydrol Derivatives and Ethyl Bromocyanoacetate. N. E. GOLDTHWAITE (*Amer. Chem. J.*, 1903, 30, 447—470).—When diphenylmethane is treated with bromine at a low temperature and in presence of iodine, the product consists of about 70 per cent. of the di-*p*-bromo-derivative, 27 per cent. of the *op*-dibromo-compound, whilst the remainder is probably the di-*o*-bromo-derivative.

Di-p-bromodiphenylmethane, $\text{CH}_2(\text{C}_6\text{H}_4\text{Br})_2$, the constitution of which was proved by its conversion into di-*p*-bromobenzophenone, is a white, crystalline compound which melts at 64°, is soluble in the usual organic solvents, and is best recrystallised from light petroleum. When this substance is heated with bromine at 150°, *di-p-bromodiphenylmethyl bromide*, $\text{CHBr}(\text{C}_6\text{H}_4\text{Br})_2$, is produced, which crystallises in slender needles, melts at 106—107°, is very soluble in alcohol, benzene, or chloroform, but less so in ether or light petroleum, and gives a deep red coloration with concentrated sulphuric acid.

Tetra-p-bromotetraphenylethylene, $\text{C}(\text{C}_6\text{H}_4\text{Br})_2 \cdot \text{C}(\text{C}_6\text{H}_4\text{Br})_2$, obtained by heating di-*p*-bromodiphenylmethyl bromide at 165°, crystallises from alcohol in small, white needles, melts at 248°, and is not affected by treatment with bromine. An attempt to effect its reduction by means of zinc dust and acetic acid was unsuccessful.

When di-*p*-bromodiphenylmethyl bromide is treated with sodium acetate dissolved in glacial acetic acid, *di-p-bromobenzhydrol acetate*,

$\text{CH}(\text{C}_6\text{H}_4\text{Br})_2 \cdot \text{OAc}$, is produced, which crystallises in short, slender needles, melts at $70-72^\circ$, and is soluble in most organic solvents. *Di-p-bromobenzhydrol*, $\text{CH}(\text{C}_6\text{H}_4\text{Br})_2 \cdot \text{OH}$, prepared by the action of alcoholic potassium hydroxide on the acetate, crystallises in long, slender, white needles, melts at $115-116^\circ$, is very soluble in ether, alcohol, or acetic acid, gives a red coloration with concentrated sulphuric acid, and is converted into *di-p-bromobenzophenone* by oxidising agents. When *di-p-bromobenzhydrol* is heated gradually to 300° , *tetra-p-bromophenylethane* and *di-p-bromobenzophenone* are produced, but when heated quickly to 250° in a current of dry air, *di-p-bromobenzhydryl ether* is obtained. If the compound is heated for 40 minutes at 300° , *di-p-bromobenzophenone*, *di-p-bromodiphenylmethane*, and probably *tetra-p-bromotetraphenylethylene* are formed, whilst if it is heated at 300° for 8 hours in a stream of carbon dioxide, a mixture is obtained probably consisting of *di-p-bromobenzophenone*, *di-p-bromobenzhydryl ether*, *tetra-p-bromotetraphenylethylene*, and the corresponding ethane derivative.

Di-p-bromobenzhydryl ether, $\text{O}[\text{CH}(\text{C}_6\text{H}_4\text{Br})_2]_2$, best prepared by heating *di-p-bromodiphenylmethyl bromide* with water at 120° in a sealed tube, forms masses of short, radiating crystals, melts at $155-156^\circ$, and is readily soluble in benzene or chloroform; when heated with acetic acid, it is converted into *di-p-bromobenzhydryl acetate*.

Di-p-bromobenzhydryl ethyl ether, $\text{CH}(\text{C}_6\text{H}_4\text{Br})_2 \cdot \text{OEt}$, a viscid, colourless oil with a characteristic, not unpleasant odour, boils at 228° under 16 mm. pressure and gives a deep red coloration with concentrated sulphuric acid; when heated at 300° , it undergoes decomposition with formation of ethyl alcohol, *di-p-bromobenzophenone*, and *di-p-bromodiphenylmethane*.

Di-p-bromotriphenylmethane, $\text{CHPh}(\text{C}_6\text{H}_4\text{Br})_2$, obtained by the action of concentrated sulphuric acid on a mixture of *di-p-bromobenzhydrol* and benzene, crystallises in slender needles, melts at 100° , distils at 260° under 15 mm. pressure, and is easily soluble in all organic solvents.

The paper concludes with a detailed account of the preparation and properties of ethyl bromocyanoacetate, and the action of sodium, ethyl sodiocyanoacetate, ethyl sodioacetoacetate, ethyl sodiomalonate, and aniline on it (compare Nef, *Abstr.*, 1898, i, 107). E. G.

[Formation of] *Retene* from *Abietic Acid*. ALBERT VESTERBERG (*Ber.*, 1903, 36, 4200-4202).—Crystallised *abietic acid* was heated with half its weight of sulphur at 200° , subsequently at 250° , and distilled under about 20 mm. pressure. A small quantity of a yellow, crystalline distillate was obtained, which proved to be *retene*.

E. F. A.

Substituted Mercurammonium Iodides from Primary and Secondary Amines. MAURICE FRANÇOIS (*Compt. rend.*, 1903, 137, 1069-1070).—Mercuric iodide reacts with primary amines and their salts to give the following series of compounds: (1) mercuriodides of the general formula $(\text{NH}_2\text{R}, \text{HI})_n(\text{HgI}_2)_n$, for example, aniline mercur-

iodide $\text{NH}_2\text{Ph}\cdot\text{HI}\cdot\text{HgI}_2$; (2) mercurichloroiodides having the formula $(\text{NH}_2\text{R}\cdot\text{HI})_n(\text{NH}_2\text{R}\cdot\text{HCl})_n(\text{HgI}_2)_n$, for example, aniline mercurichloroiodide, $(\text{NH}_2\text{Ph}\cdot\text{HI})_2\cdot\text{NH}_2\text{Ph}\cdot\text{HCl}\cdot\text{HgI}_2$; (3) crystalline dissociable compounds having the general formula $(\text{NH}_2\text{R})_n(\text{HgI}_2)_n$, soluble in alcohol, ether, or excess of the base. When compounds of the last series are treated with a solution of sodium hydroxide, the hydrogen of the NH_2 group is replaced by mercury, and insoluble products result. Thus diphenylmercuridiammonium iodide, $2\text{NH}_2\text{Ph}\cdot\text{HgI}_2$, gives trimercuridiphenyldiammonium iodide, $2\text{NHgPh}\cdot\text{HgI}_2$.

Tertiary amines react readily with mercuric iodide, forming compounds of the type $(\text{NR}_3)_n(\text{HgI}_2)_n$, which contain no replaceable hydrogen, and are therefore not changed by the action of a solution of sodium hydroxide. Mercuripyrityldiammonium iodide, $(\text{C}_5\text{H}_5\text{N})_2\cdot\text{HgI}_2$, can be obtained in large, colourless crystals which are not altered by prolonged contact with a 25 per cent. sodium hydroxide solution in the cold; if, however, the mixture is heated by a current of steam, the mercuripyrityldiammonium iodide dissociates into pyridine, which is volatile in the steam, and mercuric iodide, which is converted into the oxyiodide in the ordinary way.

M. A. W.

Action of Secondary Bases on the Carbonates of Phenols.

BOUCHETAL DE LA ROCHE (*Bull. Soc. chim.*, [iii], 31, 19—21).—The secondary bases of the fatty series react with the carbonates of phenols to give the corresponding carbamates, $\text{NR}_2\cdot\text{CO}_2\cdot\text{C}_6\text{H}_4\cdot\text{X}$. Dimethylamine, however, does not react in this way. *Phenyl diethylcarbamate*, is a colourless liquid, which boils at 150° under 15 mm. pressure. *o-Tolyl diethylcarbamate* is a colourless, crystalline substance melting at 52° and boiling at 178 — 179° under 15 mm. pressure. *o-Tolyl dipropylcarbamate* boils at 180° under 19 mm. pressure. *p-Tolyl dipropylcarbamate* is a colourless liquid which boils at 185° under 18 mm. pressure. *Guaiacol dipropylcarbamate* is also a liquid; it boils at 196° under 18 mm. pressure. *Phenyl dibenzylcarbamate* is a colourless oil, which distils at 282 — 284° under 23 mm. pressure. *Tolyl* and *guaiacol dibenzylcarbamates* were also prepared; they are viscous oils, which boil and decompose at above 300° under reduced pressure.

S. S.

Action of Phenylcarbimide on Certain Monohydric Alcohols. ARMAND BLOCH (*Bull. Soc. chim.*, [iii], 31, 49—53).—By the action of phenylcarbimide on monohydric alcohols of high molecular weight, the corresponding phenylurethane was obtained in every case. *n-Octyl phenylurethane*, $\text{NHPh}\cdot\text{CO}_2\cdot\text{C}_8\text{H}_{17}$, forms colourless prisms, which melt at 69° and are soluble in hot alcohol; *sec-octyl phenylurethane* is a liquid; *undecyl phenylurethane*, $\text{NHPh}\cdot\text{CO}_2\cdot\text{C}_{11}\text{H}_{23}$, melts at 55 — 55.5° and crystallises in colourless needles, soluble in light petroleum or methyl alcohol, easily so in alcohol, ether, benzene, or chloroform. *Cetyl phenylurethane*, $\text{NHPh}\cdot\text{CO}_2\cdot\text{C}_{16}\text{H}_{33}$, is deposited from alcohol in the form of crystalline scales, melts at 73° , distils at 244 — 250° under 17.5 mm. pressure, and is almost insoluble in cold alcohol or light petroleum. *Myricyl phenylurethane*, $\text{NHPh}\cdot\text{CO}_2\cdot\text{C}_{20}\text{H}_{41}$,

melts at 91.5° , is very unstable, and decomposes readily into its constituents. S. S.

Derivatives of Anilinoacetonitrile. TH. PARADIES (*Ber.*, 1903, 36, 4302—4305).—*Anilinothioacetamide*, $\text{NHPh}\cdot\text{CH}_2\cdot\text{C}(\text{:NH})\cdot\text{SH}$, prepared by the action of alcoholic ammonium sulphide on anilinoacetonitrile, melts at 165° . When heated with concentrated sulphuric acid, it did not yield indoxyl.

Anilinoacetiminoethyl ether, $\text{NHPh}\cdot\text{CH}_2\cdot\text{C}(\text{:NH})\cdot\text{OEt}$, prepared by the action of dry hydrogen chloride on an ethyl-alcoholic solution of anilinoacetonitrile, was obtained in the crude form, which was converted into the *hydrochloride* melting at 195° . The free imino-ether cannot readily be obtained from the hydrochloride; it may, however, be obtained from the nitrile and hydroxylamine hydrochloride in alcoholic solution by the addition of sodium carbonate. It boils at $115\text{--}117^\circ$ under 60 mm. pressure; its *nitroso*-derivative melts at 98° ; its *sulphate* is soluble in water with difficulty.

Anilinoethenylamido-oxime, $\text{NHPh}\cdot\text{CH}_2\cdot\text{C}(\text{:N}\cdot\text{OH})\cdot\text{NH}_2$, prepared from hydroxylamine and anilinoacetonitrile, separates from alcohol in rhombic crystals and melts at $147\text{--}148^\circ$; its *hydrochloride* melts at $174\text{--}175^\circ$. A. McK.

Phenylene- and Tolylene-diglycines. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 145062).—Glycollonitrile, $\text{OH}\cdot\text{CH}_2\cdot\text{CN}$, reacts with *p*-phenylenediamine to form *p*-phenylenediaminodiacetonitrile, $\text{C}_6\text{H}_4(\text{NH}\cdot\text{CH}_2\cdot\text{CN})_2$, which crystallises from alcohol in leaflets insoluble in water and melts at $170\text{--}171^\circ$. Dilute mineral acids or alkalis hydrolyse it to *p*-phenylenediglycine, $\text{C}_6\text{H}_4(\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$, which is insoluble in cold water, but dissolves in dilute acids or alkalis, and separates from a large excess of hot water in crystals melting and decomposing at $233\text{--}235^\circ$. The dinitrile dissolves in concentrated sulphuric acid forming *p*-phenylenediaminotiacetamide, $\text{C}_6\text{H}_4(\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2)_2$, which separates in crystals on pouring the solution on to ice, and melts and decomposes at $270\text{--}275^\circ$; it is hydrolysed to *p*-phenylenediglycine by prolonged boiling with dilute solutions of the alkali hydroxides.

Hydrogen cyanide and formaldehyde may be employed in place of glycollonitrile. The *p*-phenylenediamine may be conveniently combined with formaldehyde to form a bluish-white, pulverulent compound, insoluble in water or alcohol, but dissolving in solutions of alkali hydrogen sulphites and melting and decomposing at 235° . Potassium cyanide reacts with a solution of the alkali hydrogen sulphite compound, giving a quantitative yield of phenylenediglycine.

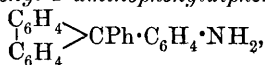
p-Phenylenediglycine melts at $150\text{--}160^\circ$, and *p*-tolylenediaminodiacetonitrile at $100\text{--}103^\circ$. C. H. D.

Preparation of Phenylglycine and its Homologues. BASLER CHEMISCHE FABRIK (D.R.-P. 145376. Compare preceding abstract).—An alkaline alcoholic solution of methylenedianiline, $\text{CH}_2(\text{NHPh})_2$, prepared by the condensation of aniline with formaldehyde (Eberhardt and Walter, *Abstr.*, 1894, i, 451), reacts with potassium cyanide to form phenylglycine, ammonia being evolved. The yield is almost

quantitative. The homologues of phenylglycine may be prepared in a similar manner. C. H. D.

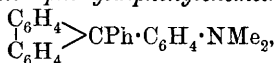
4:5-Dinitro- α -naphthylamine. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 145191).—5-Nitro- α -acetonaphthalide, prepared by heating 5-nitro- α -naphthylamine with acetic acid and acetic anhydride, or by adding acetic anhydride to an aqueous suspension of nitronaphthylamine at 50–70°, crystallises from acetic acid in thick, brown prisms giving a bright yellow powder and melting at 220°. The *formyl* derivative is formed with great ease on merely warming the amine with formic acid, and crystallises in small, yellow needles melting at 199°. Nitration with nitric and sulphuric acid yields the *dinitro*-compound, crystallising from boiling glacial acetic acid in felted, yellow needles melting at 244°. 4:5-Dinitro- α -naphthylamine, prepared by the hydrolysis of the acetyl derivative with dilute sulphuric acid, crystallises from acetic acid in brownish-orange leaflets melting at about 236°. C. H. D.

Derivatives of Diphenylenediphenylmethane. FRITZ ULLMANN and R. VON WURSTENBERGER (*Ber.*, 1904, 37, 73–78).—*Phenyl-diphenylenecarbinol*, $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{CPh} \cdot \text{OH}$, prepared from fluorenone and magnesium phenyl bromide, separates from light petroleum in transparent crystals, melts at 107°, and is easily reduced by zinc and acetic acid to phenyldiphenylenemethane, identical with Hemilian's product (*Abstr.*, 1878, 431). The carbinol readily condenses with bases when boiled with them. *Phenyl-4'-aminophenyldiphenylenemethane*,



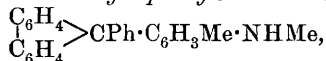
prepared from aniline, crystallises from dilute alcohol, melts at 179°, and gives a crystalline *hydrochloride* which decomposes at 220–230°; the *acetyl* derivative crystallises from benzene and melts at 213.5°. *Diphenyldiphenylenemethane-4'-azodimethylan line*, prepared from the diazonium salt of the base and dimethylamine, forms large, red leaflets and melts at 192°.

Phenyl-4'-dimethylaminophenyldiphenylenemethane,



prepared by condensing the carbinol with dimethylaniline, crystallises from a mixture of benzene and light petroleum in stellate aggregates of large, slightly-coloured prisms and melts at 141.5°.

Phenyl-4'-methylamino-3'-tolylidiphenylenemethane,



prepared from methyl-*o*-toluidine, crystallises from the same mixture in large, lustrous prisms and melts at 190.5°; the *hydrochloride* melts at 140–146° and decomposes at 160°.

Phenyl-4'-hydroxyphenyldiphenylenemethane, $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{CPh} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$,

obtained by adding concentrated sulphuric acid gradually to a solution of diphenylenephenylcarbinol and phenol in glacial acetic acid,

crystallises in a colourless, asbestos-like mass of needles and melts at 191°.

W. A. D.

Additive Compounds with Dimethylaniline. C. LORING JACKSON and LATHAM CLARKE (*Ber.*, 1904, 37, 176—178. Compare Hepp, *Abstr.*, 1883, 315).—The following additive compounds have been obtained.

1:3:5-*Trichlorotrinitrobenzene dimethylaniline* forms brownish-red prisms decomposing at 78°. 1:3:5-*Tribromotrinitrobenzene dimethylaniline*, crystallises in dark brown prisms decomposing at 50°. 3-Bromo-2:4:6-*trinitrotoluene dimethylaniline*, forms dark red prisms melting at 120°. 1:3:4:5-*Tetrachlorodinitrobenzene dimethylaniline*, forms orange-yellow prisms melting at 113°. *Ethyl 4-bromo-3:5-dinitrobenzoate dimethylaniline*, crystallises in broad, orange-red prisms melting at 56°. 1:3:5-*Tri-iododinitrobenzene dimethylaniline* forms pale yellow prisms melting at about 160°. 1:3:5-*Trianilinodinitrobenzene dimethylaniline* forms dark brown prisms melting at 120°.

The compounds are obtained by dissolving the nitro-compound in the base and adding alcohol; as a rule, they cannot be recrystallised without undergoing decomposition. They also decompose when exposed to the air.

Chloranil dimethylaniline yields an additive compound which crystallises in short, dark blue prisms melting at 105°. *Trichloroquinone dimethylaniline* forms a blue compound melting at 65°.

[Similar, but much more stable, additive products have been obtained by Sudborough (*Trans.*, 1901, 79, 522) and Hibbert and Sudborough (*ibid.*, 1903, 83, 1334)].

J. J. S.

Interaction between Nitrobenzene and Aniline in the Presence of Alkali. ALFRED WOHL (*Ber.*, 1903, 36, 4135—4138. Compare *Abstr.*, 1901, i, 612).—*p*-Nitrosodiphenylamine is obtained in addition to the products previously described when nitrobenzene and aniline are heated with finely-powdered, dry sodium hydroxide, first at 110—120° and then at 120—125°. When boiled with an aqueous solution of hydroxylamine hydrochloride, the nitroso-derivative is transformed into quinonedioxime.

The corresponding nitroso-derivative, obtained from α -naphthylamine, nitrobenzene, and an alkali hydroxide, crystallises in small, blue needles and melts at 143°.

J. J. S.

Transformation of Diphenylnitrosoamine into *p*-Nitrosodiphenylamine. H. RAKEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 267—269).—The rate of transformation of diphenylnitrosoamine into *p*-nitrosodiphenylamine was examined by a colorimetric method, advantage being taken of the fact that the nitrosoamine has a faintly yellow colour, which in dilute solutions may be neglected, whilst the nitroso-base, in combination with hydrochloric acid, forms a brown powder, the dilute alcoholic solution of which is deep yellow, and more concentrated solutions dark brown or red. The experiments were made in alcoholic solution with hydrochloric acid as catalyser.

The reaction is of the first order. The reaction constant is proportional to the concentration of the hydrochloric acid. Addition of

water causes a large fall in the value of the constant. The temperature coefficient is very great.

The transformation in question is intramolecular.

A. McK.

Action of Light on Dinitrobenzylideneaniline. FRANZ SACHS and EMIL SICHEL (*Ber.*, 1903, 36, 4373—4377).—2:4-Dinitrobenzylideneaniline, when exposed to the action of sunlight in benzene solution, forms two products, one melting at about 289°, of which the nature has not yet been established, and an orange-red substance melting at 180·5° and having the composition $C_{19}H_{14}O_3N_4$. This is shown to be *benzene-o-azo-p-nitrobenzanilide*, produced by intramolecular rearrangement of the anilide and subsequent exchange of oxygen for the group :NPh, derived from a second molecule of the benzylideneaniline, which is itself converted into dinitrobenzaldehyde; the latter substance was proved to be among the products of the reaction. E. F. A.

Direct Preparation of *cyclo*Hexanol and *cyclo*Hexanone from Phenol. PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1903, 137, 1025—1027. Compare Abstr., 1901, i, 195, 263).—When a mixture of phenol and excess of hydrogen is passed over reduced nickel at 215—230°, *cyclo*hexanol is formed, which is partially decomposed by the nickel into *cyclo*hexanone (compare Abstr., 1903, i, 454). The mixture boils at 155—165°, and cannot be separated by fractional distillation.

Pure *cyclo*hexanone is prepared by passing the vapour of the mixture over reduced copper at 330°, the ketone is not affected, and the alcohol is converted into the ketone with liberation of hydrogen; it is a colourless liquid with the odour of propanone and suggesting that of camphor; it boils at 155·5° (corr.) and is identical with the compound prepared by Baeyer (Abstr., 1894, i, 175) and Markownikoff (Abstr., 1899, i, 23).

Pure *cyclo*hexanol is obtained from the mixture by passing its vapour, mixed with excess of hydrogen, over reduced nickel at 140—150°; it solidifies under cold water, boils at 161° (corr.), and is identical with the compound prepared by Baeyer and Markownikoff (*loc. cit.*). M. A. W.

Oxidation of Mixed Organo-magnesium Compounds. Synthesis of Phenols. F. BODROUX (*Bull. Soc. chim.*, 1904, [iii], 31, 33—36).—Organo-magnesium compounds, $R \cdot MgX$, rapidly absorb oxygen, forming substances of the general formula $RO \cdot Mg \cdot X$, which are decomposed by acids with liberation of a phenol or an alcohol. The present paper deals only with the oxidation of aromatic magnesium compounds and the preparation of the corresponding phenols. Air is bubbled through the ethereal solution of an organo-magnesium haloid until it becomes greenish-black in colour; the phenol may then be extracted with an aqueous alkali hydroxide. The following phenols were synthesised, the figures in brackets giving the yields: phenol (18 per cent.), *o*-cresol (20 per cent.), *p*-cresol (15 per cent.), α -naphthol (12 per cent.), *p*-methoxyphenol (12 per cent.), *p*-ethoxyphenol (10 per cent.), 4-bromo- α -naphthol (22 per cent.), and 4-chloro- α -naphthol (21 per cent.). S. S.

A New Tri-iodophenol. P. BRENANS (*Compt. rend.*, 1903, 137, 1065—1067. Compare Abstr., 1901, i, 643; 1902, i, 280).—2:3:5-Tri-iodo-1-nitrobenzene, obtained in the usual way from 4:6-di-iodo-2-nitroaniline, crystallises in large, yellow prisms melting at 124°, is soluble in hot alcohol or methyl alcohol, and more so in the other ordinary solvents; it is reduced by stannous chloride to 2:3:5-tri-iodoaniline, which crystallises in colourless, silky needles melting at 116°, slightly soluble in ether or light petroleum, more so in benzene, alcohol, or acetic acid; its *acetyl* derivative crystallises in thin, silky needles which partially volatilise at 200° and melt at 227°; it is only slightly soluble in organic solvents. 2:3:5-Tri-iodophenol, prepared by diazotising 2:3:5-tri-iodoaniline, melts at 114° and is very soluble in organic solvents, but can be crystallised from a mixture of benzene and light petroleum; the *ethyl* ether, $C_6H_2I_3 \cdot OEt$, crystallises in thin, colourless, silky needles melting at 120°; the *acetyl* derivative forms colourless needles melting at 123° and is soluble in hot alcohol or acetic acid.

M. A. W.

Preparation of 2-Nitroresorcinol. HUGO KAUFMANN and ERWIN DE PAY (D.R.P. 145190).—2-Nitroresorcinol is readily prepared by nitrating resorcinol-4:6-disulphonic acid at a low temperature. Resorcinol is dissolved in fuming sulphuric acid by warming, and after cooling to 0° a mixture of fuming sulphuric acid and nitric acid is added. When the mass has dissolved, water is added, and the nitroresorcinol is distilled in a current of superheated steam. The product obtained from acetometanilic acid is 4-nitroresorcinol.

C. H. D.

Action of Chlorosulphonic Acid on Guaiacol. AUGUSTE LUMIÈRE and LOUIS LUMIÈRE and F. PERRIN (*Bull. Soc. chim.*, 1903, [iii], 29, 1228—1229).—When a well-cooled solution of guaiacol in chloroform is treated with chlorosulphonic acid, there is first formed *o*-methoxyphenyl hydrogen sulphate (the crystalline barium salt of this was prepared), but if the mixture be allowed to remain even for a few minutes, a white, crystalline, deliquescent precipitate of *guaiacolmonosulphonic acid* is produced.

T. A. H.

Oxidation of Guaiacol by Laccase. GABRIEL BERTRAND (*Compt. rend.*, 1903, 137, 1269—1272).—The compounds most readily oxidised by laccase are those of the cyclic series containing at least two OH or NH_2 groups situated in the ortho- or para-positions with reference to one another. Quinol is oxidised by laccase to quinone. The colour change effected in guaiacol by the juice of different fungi observed by Bourquelot (Abstr., 1897, ii, 66) is due to an oxidation brought about by the laccase which is present in the juice. The oxidation product is a *tetraguaiacquinone* having the constitution
$$\begin{array}{c} O \cdot C_6H_3(OMe) \cdot C_6H_3(OMe) \cdot O \\ | \qquad \qquad \qquad | \\ O \cdot C_6H_3(OMe) \cdot C_6H_3(OMe) \cdot O \end{array}$$
; it is a fine, crystalline powder having a purplish-red colour with a faint green metallic lustre, insoluble in water, slightly soluble in ether, a little less so in alcohol, still less so in benzene, readily so in chloroform and acetic acid; all the solutions have the same mahogany-red colour and water reprecipitates the solid

from acetic acid solutions in the form of dense violet-purple flakes which melt between 135° and 140° .

Tetraguaiacoquinone is soluble in alkalis, forming coloured solutions; it is reduced by zinc and acetic acid forming *tetraguaiacquinol*, $O_2[C_{12}H_6(OMe)_2 \cdot OH]_2$, which is white and melts between 115° and 120° , its *diacetyl* derivative melts at 155 — 160° and it yields a *dimethyl* derivative. M. A. W.

1:2-Anthraquinol and its Conversion into Alizarin. KASIMIR LAGODZINSKI (*Ber.*, 1903, 36, 4020—4022. Compare Abstr., 1894, i, 420; 1895, i, 544).—Zinc dust and acetic acid or other acid reducing agents reduce 1:2-anthraquinone to 1:2-anthraquinol, $C_{14}H_{10}O_2$, which crystallises from the hot filtered solution in greenish-yellow leaflets melting and decomposing at 131° , and dissolving readily in organic solvents to slightly fluorescent solutions. Oxidising agents reconvert it into the quinone; its alkaline solutions rapidly blacken in the air.

The position of the two hydroxyl groups being the same as in alizarin, the compound may be converted into alizarin by oxidation of its *diacetyl* derivative, $C_{18}H_{14}O_4$, melting at 145° , which is converted into diacetylalizarin by chromic acid. C. H. D.

Preparation of Hydroaromatic Alcohols. LÉON BRUNEL (*Compt. rend.*, 1903, 137, 1268—1269. Compare Abstr., 1903, i, 695).—The paper contains the results already obtained by the author on the direct hydrogenation of substituted phenols in the presence of reduced nickel (compare Sabatier and Senderens, this vol., i, 156).

Phenol is converted almost quantitatively into *cyclohexanol*, $C_6H_{11} \cdot OH$, when the liquid phenol is allowed to enter the tube containing the nickel at the rate of 12 grams per hour, with a current of hydrogen of 250 c.c. per minute, the tube being heated at 170 — 175° .

Under similar conditions, thymol is converted into *hexahydrothymol*, $C_{10}H_{19} \cdot OH$, the temperature of the tube being 180 — 185° . Hexahydrothymol is a syrupy, colourless liquid with an odour of mint, insoluble in water, soluble in alcohol or acetic acid, much less dense than water, and boiling at 214° under normal pressure.

Carvacrol is readily hydrogenated in the presence of reduced nickel at 195 — 200° ; the product is *hexahydrocarvacrol*, $C_{10}H_{19} \cdot OH$, which is a syrupy, colourless liquid with an odour suggesting that of thyme; it is insoluble in water, soluble in alcohol, less dense than water, and boils at 218 — 219° under the ordinary pressure. M. A. W.

Phenylacetylcarbinol. E. CARAPELLE (*Gazzetta*, 1903, 33, ii, 261—264).—*Phenylacetylcarbinyl acetate*, $CH_3 \cdot CO \cdot CHPh \cdot OAc$, prepared by the interaction of phenylbromoacetone, $CH_3 \cdot CO \cdot CHPhBr$, with potassium acetate in absolute alcohol, is a yellow liquid which boils at 165 — 170° under 40 mm. pressure, and is hydrolysed by barium carbonate suspended in water, giving *phenylacetylcarbinol*, $CH_3 \cdot CO \cdot CHPh \cdot OH$; this boils at 135° under 40 mm. pressure, reduces Fehling's solution and ammoniacal silver nitrate, and interacts with phenylhydrazine giving an *osazone* melting at 152 — 153° . When the foregoing acetate is hydrolysed with aqueous barium hydroxide, an intractable oil is obtained; a condensation product

similar to that obtained from acetylcarbonyl acetate by Peratoner and Leonardi (Abstr., 1900, i, 551) could not be isolated. W. A. D.

Crystallographic Characteristics of Isomeric Halogen and Nitro-derivatives of Benzoic Acid. F. M. JAEGER (*Chem. Centr.*, 1903, ii, 1173—1175; from *Zeit. Krist. Min.*, 38, 279—301. Compare Abstr., 1903, i, 240).—The original paper contains the results of crystallographic measurements of isomeric halogen and nitro-derivatives of benzoic acid collected from various sources, together with a large number of measurements of compounds not hitherto examined. The abstract contains only the latter. The isomeric chloro-nitro-acids which have the least equivalent volumes have also the most symmetrical crystalline forms. When several isomeric derivatives are formed simultaneously in certain chemical reactions, the crystalline forms of these substances usually appear to have the same symmetry and similar parameters. In the series of derivatives of 4-chloro-3-nitrobenzoic acid, successive substitution in the carboxyl group causes elongation of the crystals in the direction of the *a* and *b* axes, but decrease along the *c* axis, finally attaining a limit in the methylamide; the substitution of two H atoms in the NH₂ group by CH₃ groups has, however, an opposite effect. The crystalline forms of the derivatives of the 2:4:6-trichloro-3-nitro-acid do not show any similar relationship. E. W. W.

Chlorination of Benzoic Acid. WILHELM LOSSEN (D.R.-P. 146174).—In the chlorination of benzoic acid by ordinary methods, the *meta*-isomeride is almost exclusively obtained. The *ortho*- and *para*-isomerides may be obtained by acting on benzoic acid with a dilute solution of a hypochlorite or with molecular proportions of alkali hydroxide and chlorine at a temperature not exceeding 50°. The chlorobenzoic acids formed are separated by fractional precipitation with dilute hydrochloric acid. The *meta*- and *para*-acids separate first, *o*-chlorobenzoic acid being obtained in a pure state from the last fraction. C. H. D.

Preparation of *N*-Arylanthranilic Acids. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 145189).—The halogen atom of *o*-halogenbenzoic acids reacts with aromatic bases in presence of copper powder or copper salts (compare this vol., i, 50). Thus, phenylanthranilic acid is prepared by heating potassium *o*-chlorobenzoate with aniline, copper powder, and water. *o*-Tolylanthranilic acid, from *o*-toluidine, crystallises in silvery leaflets and melts at 188—189°; *p*-tolylanthranilic acid is similar, and melts at 191—192°. *α*-Naphthylanthranilic acid crystallises from alcohol in needles melting at 205—206°, insoluble in water. *β*-Naphthylanthranilic acid melts at 208—209°. C. H. D.

Preparation of Anthranilic Acid from Sulphoanthranilic Acid. KALLE & Co. (D.R.-P. 146716).—The sulpho-group may be removed from sulphoanthranilic acid by electrolytic reduction in neutral or slightly acid solutions, a mercury cathode and a current-density of 100—1000 amperes per sq. metre being employed.

C. H. D.

History of Anthranil. GUSTAV HELLER (*Ber.*, 1903, 36, 4178—4188. Compare Abstr., 1895, i, 524; 1902, i, 779).—Mainly a polemical reply to Bamberger (Abstr., 1903, i, 432). In support of the formula $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown NH \end{smallmatrix}$ for anthranil, the following additional facts are brought forward (compare also Heller, Abstr., 1903, i, 827). The phenylhydrazone of *o*-aminobenzaldehyde is formed by the action of phenylhydrazine on anthranil at the ordinary temperature.

Stannic chloride and a solution of anthranil in concentrated hydrochloric acid yield a crystalline precipitate of $(C_7H_5ON)_2 \cdot H_2SnCl_6$. It turns red at 195°, decomposes at 243°, and is hydrolysed by dilute hydrochloric acid.

Anthranil and benzenesulphonic chloride at 150° yield a compound, $C_{20}H_{14}O_4N_2S$, *benzenesulphodanthranil*, which crystallises from benzene in minute needles melting at 211—212°.

When methylated with methyl sulphate at the ordinary temperature, anthranil yields the pure *N*-methyl ether, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown NMe \end{smallmatrix}$, in the form of an oil, which distils at 245° with slight decomposition, or at 162° (corr.) under 40 mm. pressure. Its salts are readily soluble, but sparingly soluble double salts with stannic chloride and mercuric chloride have been obtained. The *ferricyanide* forms dark-coloured crystals, the *thiocyanate* colourless crystals, the *platinichloride* pale yellow aggregates melting and decomposing at 199—200°, and the *aurichloride* needles melting at 125—127°.

Methylantranil and phenylhydrazine at the ordinary temperature yield the *phenylhydrazone* of *o*-methylaminobenzaldehyde in the form of long, yellow needles melting at 123—124°. When heated with dilute alkali hydroxides at 150°, the methyl ether yields methylantranilic acid and methylaniline. J. J. S.

Optical Behaviour and Constitution of Nitrosoalkylurethanes and Anthranil. A Correction. JULIUS W. BRÜHL (*Ber.*, 1903, 36, 4294—4295).—Certain of the values given by the author and quoted in a previous abstract (this vol., i, 92) have been found to be erroneous. The corrected values are as follows. Nitrosoethylurethane, n_D 1.43676; M_D 35.12. Nitrosomethylurethane, n_D 1.43905; M_D 30.45. Anthranil, n_D 1.58452; M_D 33.70. Methylantranil, n_D 1.57795; M_D 38.94. A. McK.

Unsaturated Compounds. I. Action of Hydroxylamine on Unsaturated Acids. THEODOR POSNER (*Ber.*, 1903, 36, 4305—4318).—The different unsaturated acids were caused to interact with freshly prepared free hydroxylamine in alcoholic solution, either at the ordinary temperature or at the boiling point. *α*-Hydroxylamino- β -phenylpropionic acid, $CH_2Ph \cdot CH(NH \cdot OH) \cdot CO_2H$, obtained from cinnamic acid, separates from alcohol as a white, lustrous, crystalline powder and melts and decomposes at 165°. When reduced, it gives phenylalanine (*infra*), and on oxidation with ammoniacal silver nitrate is converted into a compound, $C_9H_7O_2N$, which crystallises from benzene in colourless, silky needles melting at 148—150°. When ethyl cinnamate interacts with hydroxylamine solution at the ordinary

temperature, a colourless compound is formed which, after two crystallisations from alcohol, melts at 114—115°, and on further crystallisation undergoes decomposition; analyses point to the formula $C_7H_{12}N_2O_3$, although this is improbable, because the substance is easily oxidised by ammoniacal silver nitrate to the foregoing compound, $C_9H_7O_2N$. Moreover, when warmed with water, it evolves carbon dioxide and nitrogen, and is converted, with an excellent yield, into phenylalanine (α -amino- β -phenylpropionic acid), which melts at 231°, not at 261° as stated by Erlenmeyer and Lipp (Abstr., 1882, 971); it was characterised by its copper salt and benzoyl derivative. On replacing the amino-group of phenylalanine by the hydroxyl radicle, β -phenyl- α -lactic acid, $CH_2Ph \cdot CH(OH) \cdot CO_2H$, is obtained, which crystallises from chloroform and melts at 96°.

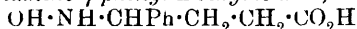
α -Hydroxylamino- β -phenylisobutyric acid,



obtained from α -methylcinnamic acid, forms nacreous leaflets, and on recrystallisation is partly decomposed; it readily loses hydroxylamine and regenerates α -methylcinnamic acid, and on this account cannot be reduced to the corresponding amino-derivative. From ethyl α -methylcinnamate and hydroxylamine, a crystalline compound melting at 119° is obtained of undetermined constitution; it undergoes decomposition when recrystallised.

α -Hydroxylamino- α -phenylpropionic acid, $OH \cdot NH \cdot CMePh \cdot CO_2H$, prepared from atropic acid and hydroxylamine, could only be obtained as a syrup; when boiled with an excess of alcoholic hydroxylamine, it is reduced to α -amino- α -phenylpropionic acid, which is best prepared by heating atropic acid directly with an excess of the base, and melts after crystallisation from water at 233°; the amino-acid is easily converted into atrolactic acid (α -hydroxy- α -phenylpropionic acid).

*γ -(or β)-Hydroxylamino- γ -phenyl-*n*-butyric acid,*



or $CH_2Ph \cdot CH(NH \cdot OH) \cdot CH_2 \cdot CO_2H$, prepared from isophenylcrotonic acid, crystallises from chloroform in lustrous leaflets, melts at 108°, and so readily loses hydroxylamine that it cannot be converted into the corresponding amino-compound.

α -Hydroxylaminobutyric acid, $CH_3 \cdot CH_2 \cdot CH(NH \cdot OH) \cdot CO_2H$, obtained from crotonic acid, crystallises from alcohol and melts at 144°; the corresponding α -aminobutyric acid could not be obtained pure.

Fumaric and maleic acids do not interact additively with hydroxylamine, but give rise only to their hydroxylamine salts. W. A. D.

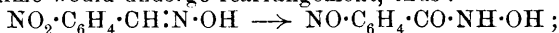
Chemical Action of Light. VII. GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1903, 36, 4266—4272. Compare Abstr., 1903, i, 562).—In their fifth communication on this subject (Abstr., 1903, i, 171), the authors examined the action of light on unsaturated compounds. Further details are now given.

The polymerisation of cinnamic acid to α -truxillic acid takes place only with the solid acid. The conversion of coumarin into dihydrocoumarin, on the other hand, occurs both with solid coumarin and with its solutions. When stilbene was exposed to light in a desiccator in the presence of air, a sublimate of benzoic acid was obtained. In accordance with Engler's views on autoxidation, the stilbene may

be regarded as forming a peroxide which suffers decomposition into benzaldehyde; the latter, then, under the influence of light is partly resinified and partly oxidised.

Maleic acid, both solid and in aqueous solution, is very slowly converted into fumaric acid in the absence of a catalyst such as bromine or iodine.

In an analogous manner to the conversion of *o*-nitrobenzaldehyde into *o*-nitrosobenzoic acid studied by the authors, *o*-nitrobenzylidene-aniline is converted into *o*-nitrosobenzanilide (Sachs and Kempf, Abstr., 1902, i, 682). On those grounds, it was expected that nitrobenzaldoxime would undergo rearrangement, thus:



it was found, however, that the *anti*-oxime was transformed into the *syn*-oxime,
$$\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\underset{\text{OH}\cdot\text{N}}{\underset{|}{\text{C}}}\cdot\text{H} \rightarrow \text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\underset{\text{N}\cdot\text{OH}}{\underset{|}{\text{C}}}\cdot\text{H}$$
 the nitro-grouping

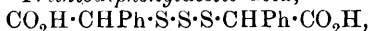
taking no part in the action. The transformation is that of the maleinoid into the fumaroid type, and is an interesting instance of a confirmation of the stereochemical theory of the isomerism of oximes.

anti-o-Nitrobenzaldoxime, melting at 102—103°, was converted into *syn o*-nitrobenzaldoxime, melting at 148—150°. *anti-p*-Nitrobenzaldoxime, melting at 128.5—129°, was converted into *syn-p*-nitrobenzaldoxime, melting at 174°, the conversion in this case taking place more readily than with the *o*-compound. On the other hand, *m*-nitrobenzaldoxime, melting at 121°, suffered no transformation. Benzene was the solvent used in each case.

It is suggested that the *m*-oxime, melting at 121°, prepared from *m*-nitrobenzaldehyde, is the stable *syn*-oxime. The *anti*-oxime, prepared by the Beckmann method, is the unstable maleinoid form, which is converted by light into the stable *syn*-form.

The esterification of opianic acid by ethyl alcohol takes place in the absence of light (compare Abstr., 1903, i, 563), but not so quickly as in sunlight. A. McK.

Preparation of Aromatic Thio-acids and their Amides. CELSO ULPANI and U. CIANCARELLI (*Atti R. Accad. Lincei*, 1903, [v], 12, ii, 219—228).—*Trithiodiphenylacetic acid*,



prepared by passing hydrogen sulphide (3 mols.) into a 10 per cent. solution of benzoylformic acid (2 mols.), forms white, triangular prisms, terminated at both ends by pyramids with slightly rounded angles, melting at 145—148°. With zinc and hydrochloric acid, it yields phenylacetic acid and hydrogen sulphide; bromine oxidises it to benzoic acid.

Thiolphenylacetic acid, $\text{SH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$, obtained in the form of its potassium salt by the action of potassium hydroxide on trithiodiphenylacetic acid, is an oil slightly soluble in water and readily so in alcohol or ether; it reduces ferric chloride to the ferrous compound yielding a blue solution, whilst with excess of the ferric salt it gives a flocculent, yellow precipitate.

Dithiophenylacetic acid, $\text{CO}_2\text{H}\cdot\text{CHPh}\cdot\text{S}\cdot\text{S}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$, separated from the blue solution yielded by the action of ferric chloride on thiolphenylacetic acid, is deposited from ether in crystals melting at

198—200°; when treated with zinc and hydrochloric acid, it gives thiophenylacetic acid.

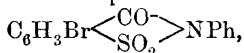
Trithiodiphenylacetamide, $S_3(CHPh \cdot CO \cdot NH_2)_2$, prepared by the action of hydrogen sulphide on benzoylformamide, crystallises from alcohol, with $1H_2O$, in microscopic, fragile aggregates of three rhombic prisms terminated by pyramids; when heated, it becomes red and melts at 217°; it is slightly soluble in acetone, ethyl acetate, light petroleum, chloroform, or carbon disulphide; potassium hydroxide hydrolyses it to thiophenylacetic acid.

T. H. P.

Chlorides of *p*-Bromo-*o*-sulphobenzoic Acid and some of their Derivatives. WILLIAM M. BLANCHARD (*Amer. Chem. J.*, 1903, 30, 485—517).—The symmetrical *chloride* of *p*-bromo-*o*-sulphobenzoic acid, $COCl \cdot C_6H_3Br \cdot SO_2Cl$, melts at 99—100°, whilst the unsymmetrical *chloride*, $C_6H_3Br \cdot \begin{smallmatrix} CCl_2 \\ \diagup \quad \diagdown \\ SO_2 \end{smallmatrix} > O$, melts at 89—90°.

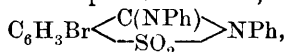
When the symmetrical chloride is treated with ammonia, it is converted into *p*-bromobenzoicsulphinide. By the action of ammonia on the unsymmetrical chloride, *p*-bromobenzoicsulphinide and ammonium *p*-bromo-*o*-cyanobenzenesulphonate are produced, the proportion of the former decreasing with dilution of the ammonia, being 26 per cent. with concentrated ammonia, 15 per cent. with dilute ammonia (1 : 3), and 6 per cent. with very dilute ammonia (1 : 20).

By the action of aniline on the symmetrical chloride at the ordinary temperature, a mixture of the anil and symmetrical anilide is produced. The *anil* of *p*-bromo-*o*-sulphobenzoic acid,



crystallises from alcohol in long, slender needles or narrow, thin plates, melts at 184·5°, and is readily soluble in benzene, chloroform, acetone, or glacial acetic acid. If the anil is heated with boiling aniline for $1\frac{1}{2}$ hours, it is converted into the symmetrical anilide. The symmetrical *anilide*, $NHPh \cdot CO \cdot C_6H_3Br \cdot SO_2 \cdot NHPh$, forms short, silky needles, melts at 236—239°, and is easily soluble in chloroform, acetone, benzene, or glacial acetic acid. When the unsymmetrical chloride is treated with aniline, a mixture of the symmetrical and unsymmetrical anilides is obtained. The unsymmetrical *anilide*, $C_6H_3Br \cdot \begin{smallmatrix} C(NHPh)_2 \\ \diagup \quad \diagdown \\ SO_2 \end{smallmatrix} > O$, crystallises in short needles, does not melt below 300°, and is only slightly soluble in the usual organic solvents.

The *dianil* of *p*-bromo-*o*-sulphobenzoic acid,



obtained by the action of phosphorus oxychloride or phosphoric oxide on either the symmetrical or the unsymmetrical anilide, crystallises from glacial acetic acid in small, bright yellow plates, melts at 199—200°, and is readily soluble in alcohol, benzene, or chloroform. If a solution of the dianil in glacial acetic acid or alcoholic potassium hydroxide is boiled for some time, the unsymmetrical anilide is produced. When the dianil is heated with concentrated hydrochloric acid, it is converted into the anil.

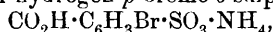
The symmetrical chloride undergoes no change when heated with

phosphorus oxychloride at 130° in a sealed tube, and neither chloride is appreciably decomposed when kept at 100° in a sealed tube for several days.

p-Bromo-*o*-cyanobenzenesulphonic acid, $\text{CN}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{SO}_3\text{H}$, is very soluble in water. When an aqueous solution of this acid is boiled for 5 hours with dilute hydrochloric acid, it remains unchanged, but when boiled for 5 hours with dilute sodium hydroxide or potassium hydroxide, the sodium or potassium *p*-bromo-*o*-carbaminebenzenesulphonate is produced, and if the boiling is continued for 10 hours longer, the corresponding *p*-bromo-*o*-sulphobenzoate is formed. Ammonium, potassium, sodium, barium, magnesium, and copper *p*-bromo-*o*-cyanobenzenesulphonates are described.

p-Bromo-*o*-carbaminebenzenesulphonic acid, $\text{NH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{SO}_3\text{H}$, was not obtained in a free state, but its sodium and potassium salts are described. When these salts are boiled for 10 hours with dilute sodium hydroxide or potassium hydroxide, they are partly converted into the corresponding *p*-bromo-*o*-sulphobenzoates.

p-Bromo-*o*-sulphaminebenzoic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{SO}_2\cdot\text{NH}_2$, obtained by heating *p*-bromobenzoicsulphinide with potassium hydroxide for 5 hours, crystallises in long, thin, lustrous plates, melts at 192 — 197° , and is readily soluble in hot water, but only slightly so in cold water. When heated at 160° , it suffers decomposition with formation of *p*-bromobenzoicsulphinide and ammonium *p*-bromo-*o*-sulphobenzoate. If the acid is heated with dilute hydrochloric acid, it is rapidly converted into ammonium hydrogen *p*-bromo-*o*-sulphobenzoate,



but if heated with dilute alkali hydroxide, this hydrolysis does not take place, even if the heating is continued for 10 hours. *p*-Bromo-*o*-sulphaminebenzoic acid may be prepared also by boiling *p*-bromobenzoicsulphinide with dilute hydrochloric acid for 45 minutes, but if the heating is continued for a longer time, ammonium hydrogen *p*-bromo-*o*-sulphobenzoate is produced. The salts of this acid are more soluble in water than the acid itself, and when heated above 150° are converted into the corresponding salts of *p*-bromobenzoicsulphinide. The calcium, strontium, barium, sodium, potassium, magnesium, and copper salts are described.

When *p*-bromobenzoicsulphinide is heated with phosphorus pentachloride in a sealed tube, *p*-bromo-*o*-cyanobenzenesulphonic chloride and *p*-bromo-*o*-chlorobenzonitrile are produced. If the temperature is not allowed to rise above 150° , the sulphonic chloride is the chief product, but if the temperature is raised to 200° , the larger proportion of the product consists of *p*-bromo-*o*-chlorobenzonitrile.

p-Bromo-*o*-cyanobenzenesulphonic chloride, $\text{CN}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{SO}_2\text{Cl}$, crystallises in white plates, melts at 82° , and is readily soluble in benzene, glacial acetic acid, or hot light petroleum. When boiled with water, it is converted into *p*-bromo-*o*-cyanobenzenesulphonic acid, and if heated with sulphuric acid, it is converted into *p*-bromo-*o*-sulphobenzoic acid.

p-Bromo-*o*-chlorobenzonitrile, $\text{C}_6\text{H}_3\text{BrCl}\cdot\text{CN}$, is volatile with steam, crystallises in white needles, melts at 51 — 61° , is very soluble in benzene, glacial acetic acid, or light petroleum, and when heated with hydrochloric or sulphuric acid is converted into *p*-bromo-*o*-chlorobenzoic acid.

E. G.

Physiological Relationships of Proteids containing Sulphur.

III. Constitution of Mercapturic Acids. ERNST FRIEDMANN (*Beitr. chem. Physiol. Path.*, 1903, 4, 486—510. Compare Abstr., 1902, i, 731; 1903, i, 75, 301; Baumann and Preusse, Abstr., 1882, 756; König, Abstr., 1892, 1090; Weiss, Abstr., 1895, i, 284; Fränkel, *ibid.*).—Baumann's *p*-bromophenylcystein or α -amino-*a-p*-bromophenylthiolpropionic acid, on treatment with nitrous acid by Jochem's method (Abstr., 1901, i, 129), yields (1) *a-hydroxy-a-p-bromophenylsulphonpropionic acid*, $C_6H_4Br \cdot SO_2 \cdot CMe(OH) \cdot CO_2H$, melting at 149° and soluble in ether; (2) *a-chloro-a-p-bromophenylthiolpropionic acid*, $C_6H_4Br \cdot S \cdot CMeCl \cdot CO_2H$, as an oil which on treatment with alkali yields hydrochloric acid and bromophenylmercaptan; (3) *a-amino-a-p-bromophenylsulphonpropionic acid*, $C_6H_4Br \cdot SO_2 \cdot CMe(NH_2) \cdot CO_2H$, crystallising in needles and melting and decomposing at 196° (compare König); and (4) a compound melting at 192° and probably an α -amino-*a-p*-bromophenylthiolpropionic acid. A better yield of the chloro-acid may be obtained by a slightly modified process, and on reduction with tin and hydrochloric acid it yields a small amount of *a-p*-bromophenylthiolpropionic acid, melting at 115 — 116° and yielding a characteristic cherry-red coloration with concentrated sulphuric acid.

The ethyl ester of the *a-chloro-a-p*-bromophenylthiolpropionic acid, on reduction with water and aluminium amalgam, yields an ester which on hydrolysis gives the same bromophenylthiolactic acid, melting at 115 — 116° . In order to determine the position of the $S \cdot C_6H_4Br$ group, the bromophenyl- α - and β -thiolactic acids have been synthesised; the β -acid, $C_6H_4Br \cdot S \cdot CH_2 \cdot CH_2 \cdot CO_2H$, is in all respects identical with the acid melting at 115 — 116° .

p-Bromophenyldiazonium chloride and potassium xanthate react, yielding an explosive additive compound, but if this is carefully decomposed by warm water, ethyl *p*-bromophenylxanthate is obtained as an oil, and on hydrolysis it yields an 87 per cent. yield of *p*-bromophenylmercaptan.

p-Bromophenyl- α -thiolactic acid, $C_6H_4Br \cdot S \cdot CHMe \cdot CO_2H$, obtained by the action of α -bromopropionic acid on the mercaptan, forms rhombic plates, sinters at 107° , melts at 112° , and gives no characteristic coloration with concentrated sulphuric acid.

p-Bromophenyl- β -thiolactic acid may be obtained by the action of bromophenylmercaptan on β -iodopropionic acid in the presence of alkali, or of *p*-bromophenyldiazonium chloride on β -thiolactic acid, and is in all respects identical with the acid melting at 115 — 116° .

The mercapturic acids are therefore not *aa*-substituted propionic acids, as suggested by Baumann, and the pyruvic acid obtained by hydrolysis is presumably formed by secondary reactions. *p*-Bromophenylcystein is thus $C_6H_4Br \cdot S \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$, and the *p*-bromophenylmercapturic acid, $C_6H_4Br \cdot S \cdot CH_2 \cdot CH(NHAc) \cdot CO_2H$. The relationship between the mercapturic acid and proteid cystein is thus extremely simple. Cystein hydrochloride forms a relatively stable additive compound with *p*-bromophenyldiazonium chloride, which on treatment with dilute sodium carbonate solution yields *p*-bromophenylcystein (16 per cent.), melting at 181° , but this, when warmed for a short time with dilute mineral acids, yields an isomeric compound

melting at 192—193° (compare Baumann). *p*-Bromophenylcystein may be converted into *p*-bromophenylmercapturic acid, melting at 152—153°, when acetylated with acetyl chloride in the presence of pyridin. The complete synthesis of mercapturic acid from cystein has thus been accomplished.

The *p*-bromophenylcystein melting at 192—193° yields an *acetyl* derivative, melting at 153—154° but not identical with bromophenylmercapturic acid. J. J. S.

Some Compounds of Bismuth with the Hydroxybenzoic Acids. PAUL THIBAUT (*Bull. Soc. chim.*, 1904, [iii], 31, 36—38).—*Bismuth p*-hydroxybenzoate, $(C_6H_5O_3)_3Bi$, forms colourless, transparent needles, and is easily decomposed by water. *Bismuthyl β-resorcyate*, $C_6H_3(OH)_2O \cdot BiO$, crystallises in transparent needles of sp. gr. 2.62 at 16°, insoluble in water and all ordinary solvents. *Bismuthyl 2:5-dihydroxybenzoate*, $C_6H_3(OH)_2 \cdot O \cdot BiO$, is obtained as pale yellow, transparent needles, which are insoluble in water. S. S.

Constitution of Aromatic Purpuric Acids. IV. Synthesis of 3:5-Dinitro-4-cyano-2-hydroxytoluene. WALTHER BORSCHKE and E. BÖCKER (*Ber.*, 1903, 36, 4357—4361. Compare Abstr., 1900, i, 645; 1902, i, 226).—The purpuric acids, prepared by the action of potassium cyanide on polynitrophenols, are oxidised to polynitrohydroxynitriles. Thus the purpurate from dinitro-*o*-cresol yields a 3:5-dinitrocyano-2-hydroxytoluene, in which the cyano-group occupies either the 4- or 6-position. The 4-cyano-compound has been prepared, and is found to be identical with the product from the purpuric acid. In the action of potassium cyanide on dinitro-*o*-cresol, it is therefore the hydrogen atom between the two nitro-groups which is replaced by the cyano-group.

4-Cyano-2-hydroxytoluene, $CN \cdot C_6H_3Me \cdot OH$, prepared by boiling the diazonium sulphate from 4-cyano-*o*-toluidine with water, crystallises from dilute alcohol in white needles and melts at 99.5°. Nitric acid of sp. gr. 1.49 converts it into 3:5-dinitro-4-cyano-2-hydroxytoluene, crystallising from dilute nitric acid in long, yellow needles and melting at 148°, identical with the product from *o*-cresolpurpuric acid. When the action of the nitric acid is interrupted after a few minutes, two mononitro-derivatives may be obtained and separated by fractional crystallisation from dilute alcohol; they then melt at 141—142° and 191—193°. 3:5-Dinitro-2-hydroxy-4-toluic acid could not be prepared from the nitrile, but is obtained by the nitration of 2-hydroxy-4-toluic acid, and crystallises from alcohol in bright yellow leaflets melting at 200°. C. H. D.

Organo-magnesium Derivatives of Monobromophenolic Ethers: Action of Carbon Dioxide. F. BODROUX (*Bull. Soc. chim.*, 1904, [iii], 31, 30—33).—Compounds of the type $OR \cdot C_6H_4 \cdot MgBr$ may be prepared by the action of magnesium on brominated phenolic ethers. Carbon dioxide decomposes these organo-magnesium bromides with formation of the corresponding acids, $OR \cdot C_6H_4 \cdot CO_2H$. In this

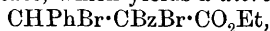
way, anisic acid and *p*-ethoxybenzoic acid were synthesised. The same reaction was carried out on the naphthalene series and led to the synthesis of 2-methoxy-*a*-naphthoic acid, 2-ethoxy-*a*-naphthoic acid, which forms colourless plates soluble in alcohol melting at 142°, and 2-propoxy-*a*-naphthoic acid, which crystallises in radiating groups of colourless needles melting at 79°. S. S.

Preparation of Indoxyl from Formylmethylantranilic Acid. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 145601).—Methylantranilic acid is converted into indoxyl by fusion with alkali (D.R.-P. 79409). Formylmethylantranilic acid, prepared by oxidation of quinoline methyl haloids, is more readily obtainable in quantity than the methyl acid, and is converted into indoxyl by fusion of its alkali salts with sodamide. The action is violent, and should be moderated by adding alkali hydroxides or cyanides to the fused mixture. The cooled mass dissolves in water and rapidly absorbs oxygen from the air, forming indigotin. C. H. D.

Preparation of Bromoindigotin. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 145910).—The preparation of bromoindigotin by the action of bromine on indigo-white (this vol., i, 57) may be modified by employing the sodium salt of indigo-white, or indigo-white itself in presence of acids or metallic salts. The yield is increased by such additions. C. H. D.

Products of the Condensation of Ethyl Benzoylacetate with Benzaldehyde. CORRADO BERTINI (*Gazzetta*, 1903, 33, ii, 145—152).—By the action of benzaldehyde (3 mols.) on ethyl diazoacetate (2 mols.), Buchner and Curtius (*Abstr.*, 1885, 1238) obtained an ethyl benzylidenebisbenzoylacetate melting at 103°, whilst the compound of the same structure prepared by Knoevenagel (*Abstr.*, 1895, i, 48) by condensing ethyl benzoylacetate with benzaldehyde in presence of diethylamine, melted at 95°. The author shows that this ester exists in tautomeric forms.

For the preparation of the ester, a mixture of an aqueous alcoholic solution of ethyl benzoylacetate (2 mols.), benzaldehyde (1 mol.), and a little piperidine was heated for an hour. The products were (1) ethyl benzylidenebenzoylacetate, which yields a dibromo-derivative,



separating from alcohol in long, shining needles melting at 110°. (2) Crystals, which, when deposited from benzene, melt and decompose at 95°, and in alcoholic solution give an intense coloration with ferric chloride; this is probably the enolic form of ethyl benzylidenebisbenzoylacetate. (3) Two other modifications of ethyl benzylidenebisbenzoylacetate, neither of which gives a coloration with ferric chloride. The first separates from alcohol in small needles melting at 132°, and has the normal molecular weight in boiling benzene; the second melts at 93—94°, but gives abnormal values for the molecular weight in boiling benzene, owing to partial decomposition into ethyl benzylidenebenzoylacetate.

Attempts were made to obtain larger quantities of the enolic (?) ester, melting at 95° , by treating the mixture of esters (3) in alcoholic solution with sodium, but the product obtained was *dehydrobenzylidenebisbenzoylacetic acid*, $\text{CHPh} \begin{smallmatrix} \text{C}(\text{CO}_2\text{H})\text{:CPh} \\ \text{C}(\text{CO}_2\text{H})\text{:CPh} \end{smallmatrix} \text{O}$, which crystallises from aqueous alcohol in shining, nacreous scales melting and decomposing at 141° ; it has the normal molecular weight in boiling benzene, and gives no coloration with ferric chloride. The *sodium, copper, and silver* salts were prepared. T. H. P.

o-Fluorenoylbenzoic Acid and its Isomeric Methyl Esters. GUIDO GOLDSCHMIEDT and ALFRED LIPSCHITZ (*Ber.*, 1903, 37,

4034—4039).—*o*-Fluorenoylbenzoic acid, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH}_2 \end{smallmatrix} \text{C}_6\text{H}_3 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, prepared by the action of phthalic anhydride on fluorene in light petroleum solution in presence of aluminium chloride, crystallises from dilute methyl alcohol or glacial acetic acid in microscopic, white needles, and melts at $227\text{--}230^{\circ}$ after sintering at 220° . Even in traces, it produces an intense reddish-violet coloration in concentrated sulphuric acid. It is a carboxylic acid of Fortner's benzoylfluorene (*Abstr.*, 1903, i, 177), but could not be converted into the ketone by distillation with lime, although distillation with zinc dust gave benzylfluorene.

The *methyl* ester, $\text{C}_{22}\text{H}_{16}\text{O}_3$, prepared by the action of methyl alcohol and sulphuric acid on the acid or of methyl iodide on the silver salt, crystallises from methyl alcohol in microscopic prisms and melts at $126\text{--}128^{\circ}$. The chloride of the acid, prepared by means of thionyl chloride, reacts with methyl alcohol, forming the same ester, and also thin, rectangular leaflets of an isomeride melting at $200\text{--}202^{\circ}$. The more fusible ester is less readily hydrolysed by potassium hydroxide than the other. The compound melting at $200\text{--}202^{\circ}$ must be regarded as the ψ -ester, and that melting at $126\text{--}128^{\circ}$ as the true ester, in accordance with the method of preparation and with the general rule that the ψ -esters of the similarly constituted *o*-aldehyde-acids have higher melting points and are more readily hydrolysed than the true esters. C. H. D.

Preparation of Diphenylamine-2:2'-dicarboxylic Acid. FARBERWERKE VORM. MEISTER, LUCIUS, and BRÜNING (*D.R.-P.* 145605).—In the preparation of anthranilic acid (see this vol., i, 50), *diphenylamine-2:2'-dicarboxylic acid* is obtained as a by-product, the proportion being greater when the reaction is carried out under pressure. The acid forms a colourless, crystalline powder melting and decomposing at about 300° , and dissolving very sparingly in water or organic solvents. The *sodium* salt is sparingly soluble in dilute sodium hydroxide. C. H. D.

Fluorescence of Naphthalic Anhydride and some of its Derivatives. LUIGI FRANCESCONI and G. BARGELLINI (*Gazzetta*, 1903, 33, ii, 129—133. Compare *Abstr.*, 1903, i, 34).—The modifications

made by Hewitt (Abstr., 1903, i, 346) in his theory of fluorescence does not bring this into accord with the facts that naphthalic anhydride fluoresces whilst phthalic anhydride does not. According to R. Meyer's theory (Abstr., 1898, ii, 105 and 275), the latter anhydride contains no fluorophore ring, but both naphthalic anhydride and naphthalimide contain the pyrone ring, which, according to this author, is one of the fluorophore groupings.

The manner in which the members of the fluorophore ring are combined is apparently without influence on the fluorescence. Thus acenaphtheneimine exhibits fluorescence, as also, although in feebler degree, do the mono- and di-oximes and the monohydrazone of acenaphthenequinone; in the latter compounds, the fluorescence increases either on long keeping or on heating, possibly on account of molecular rearrangement, for example, of the mono-oxime of acenaphthenequinone into naphthalimide.

Meyer's theory may be widened in its scope. As the introduction of one of the electro-negative groups, OH, Cl, Br, I, NO₂, diminishes the fluorescence, it may possibly be assumed that electro-positive groups, such as NH₂ and NMe₂, are capable of converting simpler groups into fluorophores.

Like colour, fluorescence depends on two factors: the presence of a special fluorophore group and the nature and position of substituting residues. Thus, most amino-compounds show a far more intense fluorescence than the corresponding hydroxyl derivatives.

T. H. P.

Parasantonide and Parasantonie Acid. I, II. and III. LUIGI FRANCESCONI (*Atti R. Accad. Lincei*, 1903, [v], 12, ii, 204—208, 267—273, 304—311).—Parasantonide, which was prepared by Cannizzaro and Valente by boiling santonic acid for a long time with glacial acetic acid, distilling off the latter, and heating the residue at 260—300°, may be obtained more easily and in better yield by substituting metasantonie for santonic acid. It separates from the ordinary solvents in rhombic crystals melting at 110°, has the normal molecular weight in freezing acetic acid or boiling alcohol, and in chloroform solution has $[\alpha]_D + 891.7^\circ$. It must be regarded as the lactone of parasantonie acid, which it yields under the action of an alkali hydroxide or hydrochloric acid, whilst also parasantonie acid is re-converted into parasantonide by means of acetic anhydride.

If, in the above-described method of preparation of parasantonide, the heating of the residue be limited to 180°, santonide, stereoisomeric with parasantonide, is obtained; this substance has $[\alpha]_D + 744.61^\circ$ and, with an alkali hydroxide or hydrochloric acid, yields *isosantonie* acid, which melts at 152°, has $[\alpha]_D - 73.92^\circ$ in chloroform solution, and forms methyl and ethyl esters melting at 69—70° and 76° respectively; the former has $[\alpha]_D - 50.2^\circ$. With acetic anhydride, *isosantonie* acid yields santonide.

Parasantoninimide, C₁₅H₁₉O₂N, obtained by saturating an alcoholic solution of parasantonide with gaseous ammonia, separates from the mother liquor in hard, shining crystals, which dissolve readily in

alcohol or acetic acid and to a less extent in ether, and melt at $216-217^{\circ}$; it dissolves in concentrated hydrochloric acid, from which it crystallises unchanged, and also in boiling concentrated potassium hydroxide, which converts it into parasantononic acid with evolution of ammonia; in alcoholic solution, it has $[\alpha]_D + 1135^{\circ}$. Its *acetyl* derivative, $C_{17}H_{21}O_3N$, crystallises from ether in shining needles melting at $169-170^{\circ}$ and dissolving readily in acetic acid or alcohol; in alcoholic solution it has $[\alpha]_D + 697.2^{\circ}$; when heated with alcoholic potassium hydroxide, it gives first the imide and then parasantononic acid.

In the cold, hydroxylamine and parasantonide interact, forming *parasantoninhydroxamic acid* (?), $C_{15}H_{21}O_4N$, which crystallises from aqueous alcohol in needles softening at 165° and melting at 180° ; it dissolves readily in alcohol or ethyl acetate, and to a less extent in ether. When heated at 100° , it loses 1 mol. H_2O , forming *oximidoparasantonin* (?), $C_{15}H_{19}O_3N$, which in alcoholic solution has $[\alpha]_D + 999.09^{\circ}$. The hydroxamic acid is stable to dilute hydrochloric acid and dissolves in cold solutions of alkaline hydroxides or carbonates, from which, even after prolonged heating, dilute acids precipitate it unchanged; its silver salt is white and blackens rapidly, even in the dark, with deposition of silver; with ferric chloride, its aqueous solution gives a transient violet coloration, which gives place to a white precipitate. By heating the hydroxamic acid or the oxime with acetic anhydride, an *anhydride*, $C_{30}H_{39}O_5N_2$, is obtained which crystallises from a mixture of acetic anhydride and ether in long, silky needles melting at 258° ; slightly soluble in ethyl acetate, more so in alcohol, but insoluble in alkali carbonate solutions. The *monoacetyl* derivative of the oxime, obtained by adding sodium nitrite solution to a glacial acetic acid solution of the oxime, separates in needles which are soluble in alcohol or ethyl acetate and melt at 176° .

Hydroxyparasantoninimide (?), $C_{15}H_{19}O_3N$, obtained by heating the isomeric oximidoparasantonin with hydrochloric acid, is soluble in ethyl acetate or alcohol, from which it separates in shining, rhombic crystals melting at 256° ; in alcohol, it has $[\alpha]_D + 200.1^{\circ}$; it is stable to boiling water and crystallises unchanged from solutions of the alkali carbonates; it does not combine with acetic anhydride, hydroxylamine, or semicarbazide, is not reduced by zinc and acetic acid, and gives no nitroso-compound. When treated with alkali hydroxides, it gives up ammonia and forms *hydroxyparasantononic acid*, $C_{15}H_{20}O_5$, which dissolves readily in water, alcohol, or ethyl acetate and slightly in ether, and crystallises from alcohol in long, stout needles melting at $189-190^{\circ}$; in alcoholic solution, it has $[\alpha]_D + 89.8^{\circ}$. Its *barium* salt is readily soluble in water. Its *methyl* ester dissolves readily in ether, alcohol, or ethyl acetate, from which it crystallises in long, stout needles melting at $138-139^{\circ}$ and having $[\alpha]_D + 36.4^{\circ}$; it does not combine with hydroxylamine or semicarbazide. The *monoacetyl* derivative, $C_{15}H_{19}O_4 \cdot OAc$, separates from ethyl acetate in crystals, melts at 207° , dissolves in alcohol, and has $[\alpha]_D + 64.3^{\circ}$ in alcoholic solution; it is soluble in water and in solutions of alkali carbonates, from which it is deposited unchanged.

When heated, hydroxylamine and parasantonide (or parasantonin-

hydroxamic acid) yield a *compound*, $C_{15}H_{18}O_9N_2$, which separates from the ordinary solvents in prisms melting at $171-172^\circ$; it is moderately soluble in ethyl acetate or alcohol, and in the latter has $[\alpha]_D - 111.9^\circ$; it dissolves in acetic anhydride, which deposits it unchanged, and in alkali carbonate solutions.

Parasantononic acid, obtained by heating parasantonide with an alkali hydroxide solution or with concentrated hydrochloric acid, is soluble in alcohol, ethyl acetate, chloroform, or carbon tetrachloride, from all of which it separates in large, rhombic crystals melting at 170° ; it has $[\alpha]_D - 98.51^\circ$ in chloroform solution; by the action on it of acetic anhydride, acetyl chloride, or phosphorus pentachloride, parasantonide is regenerated; it is an energetic acid, decomposing carbonates and being readily esterified in alcoholic solution by means of hydrogen chloride; its methyl ester melts at $183-184^\circ$ and has $[\alpha]_D - 15^\circ$, while the ethyl compound melts at 172° and has $[\alpha]_D - 99.89^\circ$.

With a solution of parasantononic acid in alkali hydroxide solution, hydroxylamine yields not an oxime, but a *compound*, $C_{15}H_{21}O_4N$, which crystallises from alcohol in shining, elongated prisms and cubiform polyhedra, and from ethyl acetate in crystals which are all cubiform; it melts and decomposes at $239-240^\circ$ and has $[\alpha]_D - 92.7^\circ$. By heating with acetic anhydride, this compound gives up water, forming an *anhydride*, $C_{15}H_{16}O_3N$, which crystallises from ether in long, slender prisms melting at $171-172^\circ$ and has $[\alpha]_D + 201.7^\circ$ in alcoholic solution; it dissolves in alkali hydroxide solution, being thereby transformed into the original compound melting at $239-240^\circ$.

Dibromoparasantononic acid, $C_{15}H_{18}O_4Br_2$, crystallises from a mixture of ether and light petroleum in mammillary masses of small prisms melting and decomposing at $176-177^\circ$; it dissolves readily in ethyl acetate or alcohol, and when treated with boiling water or with an alkaline hydroxide or carbonate it loses its bromine; in alcohol, it has $[\alpha]_D + 28.0^\circ$; reduction with zinc dust and hydrochloric acid yields parasantononic acid; saturation of the alcoholic solution with hydrogen bromide gas yields, as main product, the ethyl ester of a monobromo-acid (?), $C_{15}H_{21}O_4Br$.

Dihydroxyparasantononic acid, $C_{15}H_{20}O_6$, prepared by heating dibromoparasantononic acid with water or an alkali carbonate solution, forms shining, cubiform crystals which are readily soluble in alcohol or ethyl acetate and melt at $206-207^\circ$; it has $[\alpha]_D - 109.7^\circ$ in alcoholic solution. Its *barium* salt ($+H_2O$) is readily soluble in water.

Dehydrodihydroxyparasantononic acid, $C_{15}H_{18}O_5$, obtained by the action of an alkali hydroxide solution on dibromoparasantononic acid, separates from acetic acid in rosettes of needles and from water in microscopic, elongated prisms melting at $187-188^\circ$; it is soluble in ether or alcohol, and in the latter has $[\alpha]_D - 31.55^\circ$; its *barium* salt ($+H_2O$) which is readily soluble in water, and its *silver* salt were prepared; the *ethyl* ester is a syrupy compound. On oxidation with alkaline permanganate solution, the acid yields only oxalic acid, whilst when heated with sodium hydroxide at 250° it gives dihydroxyparasantononic acid. The chlorohydrin of *dehydrodihydroxyparasantononic acid*, $C_{15}H_{19}O_5Cl$, crystallises from alcohol in slender, shining needles which melt at $204-205^\circ$ and dissolve easily in ethyl acetate, alcohol, or water; it has

$[\alpha]_D - 23.5^\circ$ in alcoholic solution. The *chlorohydrin* of *ethyl dehydrodihydroxypparasantonate*, $C_{19}H_{27}O_5Cl$, crystallises from ethyl acetate in plates which have a fatty lustre and melt at $170-171^\circ$; it has $[\alpha]_D - 97.0^\circ$ in alcoholic solution; it is readily hydrolysed by alkaline hydroxides, giving the chlorohydrin of the acid. The chlorohydrin of the methyl ester melts at 146° and that of the benzyl ester at $129-130^\circ$. T. H. P.

Kino: an Investigation of its Constituents. The Constitution of Kino-tannic Acid. EDMUND WHITE (*Pharm. J.*, 1903, [iv], 17, 702-704).—Numerous attempts were made to obtain kino-tannic acid in a crystalline form, but without success. When the acid was heated with acetic anhydride or acetyl chloride, amorphous products were obtained. On benzoylation by the Schotten-Baumann method or by means of benzoic anhydride, no crystalline product was formed. The *methyl* derivative of kino-tannic acid was obtained as amorphous, microscopic granules containing 29.25 per cent. of methoxyl. E. G.

A Supposed Oxime of Meconic Acid. ALBERTO PERATONER and A. TAMBURELLO (*Gazzetta*, 1903, 33, ii, 233-239).—The supposed oxime of meconic acid described by Odernheimer (*Abstr.*, 1884, 1302) is really *hydroxylamine meconate*, $C_7H_4O_7 \cdot NH_2 \cdot OH, H_2O$; this is shown by analysis and by the following facts. It interacts with piperonal giving meconic acid and piperonaldoxime, and is formed by the double decomposition of sodium meconate and hydroxylamine hydrochloride; it readily reduces Fehling's solution and ammoniacal silver nitrate, and its silver, calcium, and barium salts do not contain nitrogen, but are identical with the corresponding salts of meconic acid.

Calcium meconate, $C_7H_2O_7Ca, 4H_2O$, is crystalline, and *barium meconate*, $C_7H_2O_7Ba, 3H_2O$, amorphous. W. A. D.

Preparation of Aldehydes by the Aid of Organo-magnesium Compounds. LUDWIG GATTERMANN and F. MAFFEZZOLI (*Ber.*, 1903, 36, 4152-4153).—Aldehydes may be obtained by the action of ethyl formate (3 mols.) on organo-magnesium compounds (1 mol.). The following have been prepared: benzaldehyde, *o*- and *m*-tolualdehydes, anisaldehyde, phenylacetaldehyde, α -naphthaldehyde, and "camphoraldehyde" [hydroxymethylenecamphor]. The ester is dissolved in dry ether, cooled with solid carbon dioxide and ether to -50° , and to this the well-cooled ethereal solution of the magnesium compound is added. Ice-cold hydrochloric acid is then poured in and the mixture subjected to steam distillation after removal of the ether. J. J. S.

Reactions of Nitroxyl. ANGELO ANGELI and FRANCESCO ANGELICO (*Gazzetta*, 1903, 33, ii, 239-244. Compare *Abstr.*, 1902, i, 78, 765; ii, 254).—Nitrohydroxylaminic acid is readily resolved into nitrous acid and nitroxyl, $:N \cdot OH$, which interacts additively with aldehydes, nitroso-compounds, and secondary amines.

On warming benzaldehyde with sodium nitrohydroxylamine, benzhydroxamic acid, $OH \cdot CPh \cdot N \cdot OH$, is obtained in nearly theoretical

quantity; similarly, from anisaldehyde and piperonaldehyde, the corresponding hydroxamic acids, $C_8H_9O_3N$ and $C_8H_7O_4N$, crystallising from acetone, are obtained.

From nitrosobenzene and from nitrosotoluene, the corresponding nitrosophenylhydroxylamine and nitroso-*p*-tolylhydroxylamine, of the type $R \cdot NO \cdot N \cdot OH$ or $R \cdot N(NO) \cdot OH$, are obtained by the action of the nitrohydroxylaminic acid.

Piperidine hydrochloride gives with the sodium salt of the same acid the tetrazone, $C_5H_{10}N \cdot N \cdot N \cdot C_5NH_{10}$, identical with Knorr's product from 1-aminopiperidine. Coniine gave an oil which was not analysed.

W. A. D.

Dialdehydes prepared by the Action of Aldehydes on Aromatic Hydroxyaldehydes. III. *p*- and *m*-Nitrobenzylidenedivanillin Dimethyl Ethers. M. ROGOFF (*Ber.*, 1903, **36**, 3975—3978. Compare Abstr., 1902, i, 103, 547).—*p*-Nitrobenzylidenedivanillin dimethyl ether, $NO_2 \cdot C_6H_4 \cdot CH[C_6H_2(OMe)_2 \cdot CHO]_2$, prepared by methylating the condensation product from nitrobenzaldehyde and vanillin, crystallises from dilute alcohol in microscopic prisms and melts at $186-188^\circ$ (corr.). The *tetracetate*,

$NO_2 \cdot C_6H_4 \cdot CH[C_6H_2(OMe)_2 \cdot CH(OAc)_2]_2$, is precipitated from ethyl acetate by light petroleum in felted needles, and also melts at $186-188^\circ$ (corr.).

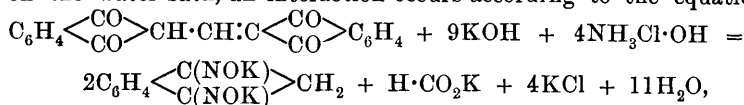
m-Nitrobenzylidenedivanillin dimethyl ether crystallises from dilute alcohol in microscopic prisms and melts at $181-183^\circ$ (corr.). The *bisphenylhydrazone*, $C_{37}H_{35}O_6N_5$, crystallises from acetic acid in microscopic needles and melts at $203.5-204.5^\circ$ (corr.).

T. M. L.

Conversion of Benzophenone into Triphenylcarbinol. RAYMOND DELANGE (*Bull. Soc. chim.*, 1903, [iii], **29**, 1131—1132).—When benzophenone is heated with potash lime, it is converted into benzene and benzoic acid (Chancel, *Annalen*, 1849, **72**, 279). The author finds that when heated with potassium hydroxide there is formed in addition a quantity of triphenylcarbinol (compare Haller and Minguin, Abstr., 1895, i, 601). The compound $OH \cdot CPh_2 \cdot OK$ appears to be first formed; this, by direct fission, gives rise to benzene and benzoic acid, whilst by interaction between two mols. of this compound, triphenylcarbinol, benzoic acid, and water are produced.

T. A. H.

Action of Hydroxylamine on Methenylbisindandione. GIORGIO ERREBA (*Gazzetta*, 1903, **33**, ii, 152—160).—If a mixture of methenylbisindandione (1 mol.), hydroxylamine hydrochloride (8 mols.), and 15 per cent. aqueous potassium hydroxide is heated for an hour on the water-bath, an interaction occurs according to the equation:

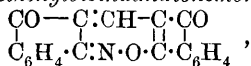


the main product being the potassium derivative of indandionedi-oxime.

If, however, the heating is stopped immediately the ketone has dis-

solved, and the liquid still retains its dark red colour, and the solution then acidified with hydrochloric acid, the products obtained are: (1) indandionedioxime, (2) a substance insoluble in water, and (3) *hydroxylaminomethyleneindandione*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}:\text{CH}:\text{NH}\cdot\text{OH}$, which crystallises from alcohol in thin, orange needles melting at 250° when heated quickly; it dissolves slightly in water or benzene, and has acid properties, being readily soluble in solutions of ammonia, or potassium or sodium hydroxide, giving liquids which do not decompose on boiling; the addition of ferric chloride to the aqueous solution produces turbidity and a brownish-green colour, which disappears on acidifying; the *potassium* salt forms red, acicular crystals, and the *silver* salt a red precipitate.

The *anhydride* of *methenylbisindandionemonoxime*,



formed, together with indandionedioxime and hydroxylaminomethyleneindandione, by the interaction of hydroxylamine hydrochloride, an alcoholic solution of sodium, and methenylbisindandione, crystallises from acetic acid in orange-red needles, which melt and decompose at 303° when rapidly heated; it is soluble in xylene, and to a less extent in alcohol or benzene. It forms a *dioxime* (or *anhydride* of *methenylbisindandionetrioxime*), $\text{C}_{19}\text{H}_{11}\text{O}_3\text{N}$, which is obtained as a yellow powder melting and decomposing at about 312° ; it is soluble to a slight extent in ordinary neutral solvents, and readily in solutions of bases; its *dibenzoyl* derivative, $\text{C}_{19}\text{H}_9\text{ON}(\text{NOBz})_2$, crystallises from pyridine in minute, orange-red needles, which melt and decompose at about 280° when rapidly heated.

The *dibenzoyl* derivative of α -*diphenylenepyridinediketoxime*, $\text{OBz}:\text{N}:\text{C} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}:\text{CH}:\text{C} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}:\text{NOBz}$, separates from pyridine solution in needles melting and decomposing at about 250° . T. H. P.

Preparation of Chloranil. OTTO N. WITT and SIEGFRIED TOECHE-MITTLER (*Ber.*, 1903, 36, 4390—4392. Compare Graebe, *Abstr.*, 1891, 1027).—A good yield of practically pure chloranil can be obtained by the following process. *p*-Nitroaniline is converted into 2:6-dichloro-4-nitroaniline, and this is reduced with tin and hydrochloric acid to 2:6-dichloro-*p*-phenylenediamine (*Ber.*, 1875, 8, 143). The pure compound need not be isolated, but the acid solution immediately chlorinated with potassium chlorate. J. J. S.

Action of Aniline on Tetrabromo-*o*-benzoquinone. C. LORING JACKSON and HORACE C. PORTER (*Amer. Chem. J.*, 1903, 30, 518—537. Compare Jackson and Koch, *Abstr.*, 1901, i, 597).—Hexabromo-*o*-dihydroxycatechol ether melts at 304 — 307° and crystallises from nitrobenzene in iridescent scales; its *monobenzoyl* derivative is a white, crystalline substance melting at 316 — 318° .

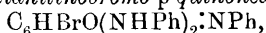
When hexabromo-*o*-quinocatechol ether is heated with hydrobromic acid at 100° in a sealed tube, it undergoes decomposition with forma-

tion of bromine, hexabromodihydroxycatechol ether, and a white, crystalline substance which is probably tetrabromocatechol.

When aniline is added to an alcoholic solution of tetrabromo-*o*-quinone, an additive compound of dianilinodibromo-*o*-quinone with aniline, $C_6Br_2O_2(NHPh)_2 \cdot NH_2Ph$, is first formed, which crystallises in pale brown needles and melts and decomposes at 121—124°. An additive compound with ethyl alcohol, $C_6Br_2O_2(NHPh)_2 \cdot EtOH$, is also obtained, which forms yellow plates and melts and decomposes at 142°; the corresponding compound with methyl alcohol melts and decomposes at 144—145°.

*Dianilinodibromo-*o*-quinone*, $C_6Br_2O_2(NHPh)_2$, prepared by repeatedly digesting its aniline compound with a mixture of benzene and light petroleum, crystallises in dark reddish-purple needles, melts at 160°, and is readily soluble in benzene, glacial acetic acid, or acetone.

If dianilinodibromo-*o*-quinone or one of its additive compounds is left with a mixture of aniline and alcohol or boiled for a few minutes with such a mixture, *dianilinobromo-*p*-quinoneanil*,



is produced, which crystallises in brilliant, jet black plates, melts at 173°, and is freely soluble in benzene, glacial acetic acid, or acetone; this compound was first obtained by Zincke (Abstr., 1887, 808), but was not analysed by him. When dianilino-*p*-bromoquinoneanil is treated with an ethereal solution of sulphur dioxide, it is converted into dianilino-*p*-quinoneanil melting at 202—203°.

If dianilinodibromo-*o*-quinone is reduced by means of a dry ethereal solution of sulphur dioxide, a substance is produced which forms rosettes of small, green needles and melts at 186—188°; if, however, a moist ethereal solution is employed, other products are obtained which have not yet been completely examined.

When hexabromo-*o*-quinocatechol ether is treated with aniline, the same products are obtained as in the case of tetrabromo-*o*-quinone.

E. G.

Action of Methyl Alcoholic Potash on 2-Nitronaphthalene.

JAKOB MEISENHEIMER and KLAUS WITTE (*Ber.*, 1903, 36, 4164—4174. Compare Abstr., 1902, i, 795).—2-Nitronaphthalene is not affected by cold methyl alcoholic potash, but with the concentrated alkali for 4 or 5 hours at 55° a considerable amount goes into solution, and when the clear liquid is acidified, β -naphthaquinone-2-oxime is obtained. It melts at 162—164°, and not at 147—148° (Worms, Abstr., 1883, 69), or at 152° (Goldschmidt, *ibid.*, 1884, 1137).

The benzoyl derivative melts at 189—190°, and not at 162°. The *p*-nitrobenzyl derivative crystallises in long, yellow needles melting at 199°.

β -Naphthaquinone-2-oxime-dimethylacetal, $C_{10}H_6(OMe)_2 \cdot N \cdot OH$, is obtained when the alkaline solution is diluted with ice and water and treated with carbon dioxide in place of a mineral acid. It crystallises in large, colourless plates melting at 126°, is readily soluble in most organic solvents, and on treatment with mineral acids, or even with alkalis, yields the oxime melting at 162—164°. Its methyl ether

is a liquid, its *p*-nitrobenzyl derivative melts at 97—98°, and its benzoate at 189—190°.

Other products obtained by the action of methyl alcoholic potash on 2-nitronaphthalene are 1:1-dinaphtha-2:2-*o*-diazine oxide, 2:2-azoxynaphthalene, and a product crystallising in red needles, very sparingly soluble in acetic acid, and melting and decomposing at 243°. On reduction, it yields *as*-1:2-naphthazine, and appears to be a mixture of this with oxy-derivatives. J. J. S.

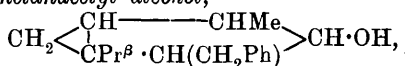
Preparation of Isomeric Sulphonic Acids by means of Catalytic Agents. M. ILJINSKY (*Ber.*, 1903, 36, 4194—4200).—When mercury or its salts are employed as catalytic agents in the sulphonation of anthraquinone, not only does sulphonation take place very much more easily, but other products are formed. Thus, besides the new *anthraquinone- α -monosulphonic acid*, which forms characteristic calcium and potassium salts and is converted on heating with milk of lime into erythroxyanthraquinone, a mixture of 1:5-, 1:8-, 1:7-, and perhaps 1:6-disulphonic acids is formed. The conditions for obtaining the 1:7-disulphonic acid in quantity are described, and the method greatly facilitates the technical production of 1:7-dihydroxyanthraquinones. E. F. A.

Preparation of Hydroxyanthraquinones. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 145238).—Nitroanthraquinones are readily converted into the corresponding hydroxy-compounds by heating with pyridine. The preparation of anthrarufin from 1:5-dinitroanthraquinone, and of chrysazin from 1:8-dinitroanthraquinone, is described. Picoline, lutidine, or collidine, or unfractionated mixtures of these bases, may be employed in place of pyridine. C. H. D.

Essence of Geranium from Cannes. PAUL JEANCARD and C. SATIE (*Bull. Soc. chim.*, 1904, [iii], 31, 43—49).—The influence of atmospheric conditions on the composition of the essence obtained from the leaves of *Pelargonium odoratissimum* has been studied. The effect of cold nights is to diminish the proportion of alcohols in the essence, but this diminution is not accompanied by a more active esterification; it is therefore due to a decrease in the amount of essence contained in the leaf. The amount of geraniol and citronellol varies; the former decreases, whilst the latter increases in cold weather. The physical constants, rotatory power, specific gravity, solubility, and viscosity do not vary much. S. S.

Constitution of Tanacetone [Thugone], $C_{10}H_{16}O$. FRIEDRICH W. SEMMLER (*Ber.*, 1903, 36, 4367—4372. Compare *Abstr.*, 1900, i, 240, 452, 676).—*Benzylidenetanacetone*, $CH_2 < \begin{matrix} CH & \text{---} & CHMe \\ | & & | \\ CPr^{\beta} & \cdot & C(CHPh) \end{matrix} > CO$, prepared by condensing tanacetone with benzaldehyde in presence of sodium ethoxide, boils at 178° under 9 mm. pressure; on oxidation, it is quantitatively decomposed into benzoic acid and homotanacetonedicarb-

oxylic acid, $\text{CH}_2 \begin{array}{c} \text{CH} \cdot \text{CHMe} \cdot \text{CO}_2\text{H} \\ | \\ \text{CP}_{1\beta} \cdot \text{CO}_2\text{H} \end{array}$, which melts at 148° and forms an anhydride, $\text{C}_{10}\text{H}_{14}\text{O}_8$, boiling at $157\text{--}158^\circ$ under 15 mm. pressure. Dihydrobenzylidenetanacetyl alcohol,



formed from the ketone by reduction with sodium and alcohol, is fully saturated; it boils at $181\text{--}182^\circ$ under 15 mm. pressure. Dihydrobenzylidenetanacetone, $\text{C}_{17}\text{H}_{22}\text{O}$, formed from this by oxidising with chromic acid, boils at the same temperature; the semicarbazone melts at 195° , and the amine boils at $185\text{--}190^\circ$ under 25 mm. pressure. Benzylidenetanacetonehydroxylamine, $\text{C}_{17}\text{H}_{20}\text{O}_2 \cdot \text{NH}_2 \cdot \text{OH}$, boils at $138\text{--}140^\circ$.
E. F. A.

Fate of Cyclic Terpenes and Camphor in the Animal System.

IV. Behaviour of Sabinol. EMIL FROMM and PAUL CLEMENS (*Zeit. physiol. Chem.*, 1903, 45, 251—262. Compare Abstr., 1902, ii, 159, 341; 1903, i, 429).—The compound previously described as sabinolglycuronic acid is best obtained by treating the urine, after ingestion of sabinol, with basic lead acetate, when a mixture of a basic lead salt with basic lead chloride is obtained; this is then decomposed with barium sulphide solution, and ultimately carefully neutralised with dilute sulphuric acid. The barium salt has not the composition of barium sabinolglycuronate, and the acid obtained by hydrolysis with sulphuric acid does not give Neuberg's test for glycuronic acid (Abstr., 1901, i, 66); it is probably a penturonic acid, $\text{C}_5\text{H}_8\text{O}_6$. Its anhydride begins to turn brown at 145° , and melts at about 168° , is fairly readily soluble in alcohol, and yields a semicarbazide melting and decomposing at 205° .
J. J. S.

Sugar Components of Solanin and Convallamarin. EMIL VOTOČEK and R. VONDRÁČEK (*Ber.*, 1903, 36, 4372—4373. Compare Abstr., 1903, i, 570; also Zeisel and Wittmann, this vol., i, 80).—Solanin and convallamarin contain dextrose, rhamnose, and a hexose of which the phenylmethylhydrazone melts at $187\text{--}188^\circ$. This is shown to be identical with galactose, the phenylmethylhydrazone of which Lobry de Bruyn and van Ekenstein found to melt at 180° ; it is now shown, however, that it melts at 188° .
E. F. A.

Action of Hydrochloric Acid on Artemisin. PASQUALE BERTOLO (*Atti R. Accad. Lincei*, 1903, [v], 12, ii, 273—278. Compare Abstr., 1901, i, 718, and 1902, i, 814).—The action of concentrated hydrochloric acid on artemisin gives rise to a compound, $\text{C}_{15}\text{H}_{16}\text{O}_3$, termed by the author *artemismic acid*, which is very soluble in alcohol, ether, light petroleum, or dilute acetic acid, and crystallises from the last-named in shining needles melting at $135\text{--}136^\circ$; it has the normal molecular weight in freezing acetic acid, and has $[\alpha]_D + 70.4^\circ$ in alcoholic solution; the barium (soluble in water), silver, lead, copper, and mercuric salts were prepared; the methyl ester was obtained as a

dense oil very readily soluble in the ordinary organic solvents. The *ethyl* ester separates from light petroleum in hard, transparent prisms, which melt at 97—98°, and dissolve in alcohol, ether, or ethyl acetate; it is insoluble in alkali carbonate solutions, but dissolves in cold potassium hydroxide solution, from which carbon dioxide reprecipitates it; it gives no oxime or phenylhydrazone, but forms a benzoyl derivative. This behaviour indicates that the ethyl ester contains a phenolic hydroxyl group, the presence of which is confirmed by the action on artemisic acid of fused potassium hydroxide, which yields *p*-dimethylnaphthol. The latter is only obtained from those derivatives of santonin or artemisin which contain such a hydroxyl group (Abstr., 1903, i, 261).
T. H. P.

Substances accompanying the Oil in Sesamé Seeds. FRANCESCO CANZONERI and F. PERCIABOSCO (*Gazzetta*, 1903, 33, ii, 253—260. Compare Villavecchia and Fabris, Abstr., 1898, i, 445).—By a process of fractional extraction and crystallisation using various solvents, the authors have isolated, in addition to sesamin and the alcohol resembling cholesterol, a substance X, which crystallises from light petroleum in nacreous laminae, melts at 91—92°, and is not changed when boiled with concentrated alkalis; its composition may be expressed by any of the formulæ $C_{23}H_{24}O_7$, $C_{22}H_{22}O_7$, $C_{13}H_{14}O_4$. It is readily attacked by cold concentrated hydrochloric acid, forming a red oil which gives in a marked degree the colour reaction with furfuraldehyde characteristic of oil of sesamé, and reduces immediately ammoniacal silver nitrate; when exposed to the air, it is oxidised to a substance which crystallises from alcohol in lustrous plates and melts at 185—186°.

The substance which Villavecchia and Fabris considered to have the composition $C_{25}H_{44}O \cdot H_2O$, contrary to their statements does not lose its water in a vacuum over sulphuric acid, but only after six hours' heating at 110°; dried at this temperature, it has the composition, $C_{26}H_{44}O \cdot \frac{1}{2}H_2O$, of an *ischolesterol*.
W. A. D.

Does Capaloin contain Methoxyl? [ALEXANDER TSCHIRCH and] K. G. v. KÜYLENSTJERNA (*Arch. Pharm.*, 1903, 241, 689—690. Compare Abstr., 1901, i, 602).—Portions of a crude specimen of capaloin were recrystallised respectively from methyl alcohol, ethyl alcohol, and acetone, and were examined by Zeisel's method; they contained 9.76, 9.38, and 9.44 per cent. of methoxyl respectively. The formula $C_{15}H_{13}O_6 \cdot OMe$ requires 9.68 per cent. Léger's inability to detect methoxyl in the substance is thus left unexplained.

C. F. B.

Brazilin from Brazilein. JOSEF HERZIG and JACQUES POLLAK (*Ber.*, 1903, 36, 3951—3953).—In preparing the triacetyl derivative, $C_{16}H_9O(OAc)_3$, already known, by reductive acetylation (Abstr., 1902, i, 482), acetylbrazeilin was obtained to the extent of about 12 per cent. of the brazilein employed. This fact, which indicates a direct conversion of brazilein into brazeilin, removes the principal objection to the quinoidal formula for brazilein.
W. A. D.

Pigments of Geranium and other Plants. ARTHUR B. GRIFFITHS (*Ber.*, 1903, **36**, 3959—3961).—The pigments of the petals of geranium, helianthus, and verbenia were isolated by extracting with alcohol and evaporating the solution to dryness in a vacuum. The absorption spectra of the pigments are described.

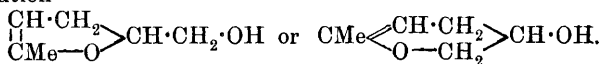
The pigments of helianthus and verbenia contain carbon, hydrogen, oxygen, nitrogen, and sulphur; to that of geranium, which is crystalline, the composition $C_{15}H_{10}O_6$ is assigned, and it yields a crystalline potassium salt, $C_{15}H_8O_6K_2$, and a diacetyl derivative crystallising from methyl alcohol in red needles and melting at 125° . This pigment in alcoholic solution has $[\alpha]_D -74.97^\circ$, whilst the specific rotations of the pigments of verbenia and helianthus are respectively -85.39° and -59.28° . All three pigments in alcoholic solution apparently emit radiations which diminish the electrical resistance of selenium. W. A. D.

Nile-blue-base as a Reagent for Atmospheric Carbon Dioxide. The Action of Acid Dyes on Cellulose, Alcohol, and Acetone, and Theory of Dyeing Histological Preparations. MARTIN HEIDENHAIN (*Pflüger's Archiv*, 1903, **100**, 217—241. Compare Abstr., 1902, i, 651, and L. Michaelis, *Pflüger's Archiv*, 1903, **97**, 634).—The author adheres to his view that the colorations of proteids are largely due to chemical causes and not mainly to physical (solid solutions), as suggested by Witt and by Michaelis. The main objections are: (1) that most of the best dyes employed are colloidal and as such would not pass (dialyse) readily into the proteid. (2) That animal tissues, although much more active than textile fabrics, are not such good solvents as compared with water. (3) That basic aniline dyes are much more readily removed by tissues from alcoholic than from aqueous solutions, although they are less soluble in water than in alcohol.

Michaelis' statement that eosin yields pale yellow solutions with benzene, toluene, xylene, and chloroform which turn a brilliant red when poured on to filter-paper is correct, but the change in colour is due to the acid action of atmospheric carbon dioxide.

Methyl and ethyl alcohols and acetone dissolve the acid to form pale yellow solutions provided no trace of carbon dioxide is present. Nile-blue-base behaves in a very similar manner, yielding reddish-brown solutions which turn blue in presence of small amounts of carbon dioxide. This reagent is a remarkably good one for carbon dioxide. The author confirms Michaelis' results on the behaviour of alcohol, acetone, and cellulose towards acid dyes. They produce with the free sulphonic acids of benzopurpurin and congo-red changes in colour similar to those produced by alkalis and by proteids. The readiness with which the change occurs depends to a large extent on the relative strength of the acid dye, and is regarded in all cases as being of a chemical nature. A kind of ester formation is suggested. Phenol, cresol, creosote, and aniline water all behave in a similar manner towards these acid dyes. The anhydrous reagents are not able to bring about the same colour changes. J. J. S.

New Syntheses effected by the Aid of Compounds containing the Methylene Group attached to One or Two Acid Radicles. Action of Epichlorohydrin on the Sodium Derivative of Acetylacetone. III. ALBIN HALLER and GEORGES BLANC (*Compt. rend.*, 1903, 137, 1203—1205. Compare Abstr., 1901, i, 538; 1903, i, 318).—By the prolonged action of epichlorohydrin on the sodium derivative of acetylacetone at the temperature of the water-bath, condensation occurs with the formation of sodium chloride, ethyl acetate, and a new alcohol, $C_6H_{10}O_2$, for which the authors suggest the constitution

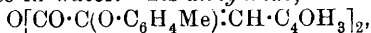


It is a colourless, mobile liquid which boils at 70° under 8 mm. pressure or at 81 — 82° under 15 mm. pressure, has a sp. gr. 0.988 at $14^\circ/4^\circ$ and n_D 1.447 at 14° ; it is very soluble in all solvents except light petroleum, and has an agreeable odour; the molecular refraction agrees with that calculated for a compound of the above constitution. The alcohol is easily resinified by alkalis and acids, and does not yield crystalline derivatives with ammonia or phenylcarbimide. The acetyl derivative, C_6H_9OAc , is a colourless liquid boiling at 190 — 195° and is insoluble in water; a hydrogenated methyl ether, $C_7H_{14}O_2$, has been prepared by the action of methyl iodide and sodium on an ethereal solution of the alcohol; it is an oil insoluble in water and boiling at 160 — 170° and having an odour resembling that of cineol.

By spontaneous change during several months, or more rapidly in the presence of traces of alkali, the alcohol is transformed into an isomeric ketone boiling at 70 — 75° under 15 mm. pressure; it has a strong odour and is insoluble in water; it forms two semicarbazides according as the condensation is effected in dilute or concentrated solutions; the former crystallises in beautiful, white needles melting at 116° and is soluble in water; the latter crystallises in small, colourless prisms melting and decomposing at 280° , and is almost insoluble in all ordinary solvents.

M. A. W.

α -m-Tolyloxy- β -furylacrylic Acid. RAFFAELE PALADINO (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1903, [iii], 9, 195—201).— α -m-Tolyloxy- β -furylacrylic acid, $C_4OH_3 \cdot CH : C(O \cdot C_6H_4Me) \cdot CO_2H$, prepared by heating furfuraldehyde (1 mol.) with sodium *m*-tolylglycolate (1 mol.) and about four times its weight of acetic anhydride, separates from 50 per cent. alcohol in masses of yellowish-white needles melting at 160 — 161° ; it is readily soluble in light petroleum, ether, or alcohol, but only slightly so in water. Its *anhydride*,



obtained by the action of phosphoric oxide on a light petroleum solution of the acid, is deposited from alcohol in minute, pale yellow crystals which are soluble in ether and melt at 149° . The *aniline* salt, $C_{14}H_{12}O_4 \cdot PhNH_2$, separates from alcohol in yellow crystals melting at 151° and soluble in light petroleum or chloroform. The *phenyl* ester, $C_{14}H_{11}O_4Ph$, is deposited from chloroform or ether in microscopic crystals melting at 151° .

T. H. P.

Phenylated Coumarones. RICHARD STOERMER [with M. REUTER]

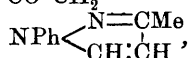
(*Ber.*, 1903, **36**, 3979—3986).—1-Phenylcoumarone, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} \text{CPh}$, prepared from salicylaldehyde, phenylchloroacetic acid, and sodium hydroxide, crystallises from dilute alcohol in silvery flakes with a faint odour of hyacinths, and melts at 120—121°. 4-Bromo-1-phenylcoumarone, $\text{C}_6\text{H}_3\text{Br} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} \text{CPh}$, prepared in a similar manner from bromosalicylaldehyde, melts at 148°. 1-Phenylcoumaran, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{smallmatrix} \text{CHPh}$, prepared by reducing 1-phenylcoumarone with sodium and alcohol or by condensing salicylaldehyde benzyl ether with sodium, solidifies to white crystals which melt at 32°; *o*-hydroxydibenzyl, $\text{HO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2\text{Ph}$, formed as a by-product in the reduction, crystallises from alcohol in white flakes and melts at 83.5°.

1-Chloro-2-phenylcoumarone, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CPh} \end{smallmatrix} \text{CCl}$, prepared by the action of phosphorus oxychloride on the lactone of *o*-hydroxydiphenylacetic acid, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CHPh} \end{smallmatrix} \text{CO}$, boils at 179° (corr.) under 13 mm. and at 191° under 18 mm. pressure; the chlorine cannot be removed by sodium amalgam, by zinc and acetic acid, or by zinc and alcoholic hydrochloric acid. Sodium and alcohol reduce the chloro-compound to 2-phenylcoumaran, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CHPh} \end{smallmatrix} \text{CH}_2$, which crystallises from hot alcohol in stout, white needles, melts at 38.5°, and boils at 167° (corr.) under 14 mm. pressure. When the preceding compound is reduced with hydrogen iodide, it gives a small yield of a phenol, $\text{C}_{14}\text{H}_{14}\text{O}$, which crystallises from alcohol and melts at 63°; the phenylurethane, $\text{C}_{21}\text{H}_{19}\text{O}_2\text{N}$, crystallises from benzene and alcohol and melts at 139°; the nature of the phenol is discussed later (Stoermer and Kippe, following page).
T. M. L.

Phosphorus Tribromide as a Reducing Agent. RICHARD STOERMER (*Ber.*, 1903, **36**, 3986—3992).—Phosphorus tribromide reduces hydroxydiphenylacetic lactone, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CHPh} \end{smallmatrix} \text{CO}$, to 2-phenyl-

coumarone, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CPh} \end{smallmatrix} \text{CH}$, deoxybenzoin to stilbene, 1-phenyl-

3-methylpyrazolone, $\text{NPh} \begin{smallmatrix} \text{N}=\text{CMe} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix}$, to phenylmethylpyrazole,

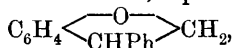


1 : 3-diphenylpyrazolone to 1 : 3-diphenylpyrazole (yield 85 per cent.), and carbostyryl in part to quinoline. In the case of 1-phenyl-

3 : 4 : 4-trimethylpyrazolone, $\text{NPh} \begin{smallmatrix} \text{N}=\text{CMe} \\ \diagup \quad \diagdown \\ \text{CO} : \text{CMe}_2 \end{smallmatrix}$, phosphorus tribromide causes the migration of a methyl group, and 1-phenyl-3 : 4 : 5-trimethyl-

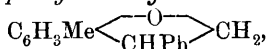
pyrazole, $\text{NPh} \begin{smallmatrix} \text{N}=\text{CMe} \\ \diagdown \quad \diagup \\ \text{CMe} \cdot \text{CMe} \end{smallmatrix}$, is produced; so also the 2-phenylcoumarone produced from the lactone referred to above is accompanied by 1-phenylcoumarone, indicating that the tribromide brings about a displacement of the phenyl group. T. M. L.

Syntheses, Isomeric Changes, and Decompositions of Phenylated Coumarones and Coumarans. RICHARD STOERMER and OTTO KIPPE (*Ber.*, 1903, 36, 3992—4013).—When heated with alcoholic potassium hydroxide at 200°, 2-phenylcoumaran,



yields ethylene, hydrogen, and a little *o*-hydroxydiphenylacetic acid (oxidation product), but is for the most part converted into the isomeric *o*-hydroxy-*aa*-diphenylethylene, $\text{CH}_2 \cdot \text{CPh} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$, a colourless oil, which boils at 167° under 13 mm., at 169—170° under 14 mm., or at 180° under 22 mm. pressure, has a sp. gr. 1.1129 at 18° and n_D 1.6193 at 18°. The sodium derivative separates on adding 30—40 per cent. sodium hydroxide to the phenol, and can be extracted by means of ether; the sodium derivative of carvacrol behaves in a similar manner. The *phenylurethane*, $\text{C}_{21}\text{H}_{17}\text{O}_2\text{N}$, crystallises from light petroleum in thin, felted needles and melts at 105°; when crystallised from dilute alcohol, the composition of the substance is unaltered, but the melting point falls to 86°, and cannot be again raised by crystallising from light petroleum. The *methyl ether*, *α-o-anisyl-α-phenylethylene* [*o*-methoxy-*aa*-diphenylethylene], $\text{CH}_3 \cdot \text{CPh} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, separates from alcohol in white needles, melts at 35°, and boils at 166° under 14 mm. pressure. It was also prepared synthetically by the action of magnesium on iodoanisole, $\text{C}_6\text{H}_4\text{I} \cdot \text{OMe}$, and acetophenone, and hydrolysis of the product by alcoholic potassium hydroxide at 200°.

1-*Chloro-2-phenyl-4-methylcoumarone*, $\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} \text{O} \\ \diagdown \quad \diagup \\ \text{CPh} \end{smallmatrix} \text{CCl}$, prepared by the action of phosphorus oxychloride on the lactone of phenyl-*p*-hydroxytolylacetic acid, crystallises in long needles, melts at 66.5°, and boils at 194° under 16 mm. pressure. It is reduced by sodium and alcohol to 2-phenyl-4-methylcoumaran,



which crystallises from alcohol in glistening, prismatic needles, melts at 57°, and boils at 184° under 18 mm. pressure. Like the lower homologue, it undergoes isomeric change when heated with alcoholic potash and is converted into *α-phenyl-α-p-hydroxytolylethylene*,



which boils at 172—174° under 10 mm. or at 187° under 20 mm. pressure, has a sp. gr. 1.0852 at 20°, n_D 1.6075 at 20°; the sodium derivative, like that just described, can be extracted by ether from the alkaline solution; the *phenylurethane*, $\text{C}_{22}\text{H}_{19}\text{O}_2\text{N}$, crystallises from light petroleum and from dilute alcohol in glistening needles, which in each case melt constantly at 101°.

2-Phenylcoumarone could not be prepared by internal condensation of phenoxyacetophenone, $\text{OPh} \cdot \text{CH}_2 \cdot \text{COPh}$, or by reducing its

1-chloro-derivative, or by the action of magnesium on *o*-bromophenoxyacetophenone, $\text{C}_6\text{H}_4\text{Br}\cdot\text{O}\cdot\text{CH}_2\cdot\text{COPh}$, but was finally synthesised from the hydroxydiphenylethylene prepared from 2-phenylcoumaran. *o*-Acetoxy-*aa*-diphenylethylene, $\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{CPh}\cdot\text{CH}_2$, boils at $172\text{--}173^\circ$ under 8 mm. or at 177° under 10 mm. pressure. The dibromide, $\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{CPhBr}\cdot\text{CH}_2\text{Br}$, crystallises from light petroleum in glistening prisms and melts at 83° . 2-Ethoxy-2-phenylcoumaran, $\text{C}_6\text{H}_4\langle\text{CPh}(\text{OEt})\rangle\text{CH}_2$, prepared by the action of sodium ethoxide on the dibromide, crystallises from hot alcohol in white, glistening flakes and melts at $88\text{--}89^\circ$.

2-Phenylcoumarone, $\text{C}_6\text{H}_4\langle\text{CPh}\rangle\text{CH}$, prepared by heating the preceding compound, boils at $177\text{--}178^\circ$ under 15 mm. or at $316\text{--}317^\circ$ (corr.) under 760 mm. pressure, has a sp. gr. 1.1449 at 19° , n_D 1.6313 at 20° , and solidifies to a crystalline mass which melts at $12\text{--}13^\circ$; a modification melting at 42° is sometimes produced and the "dimorphism" is compared with that of benzophenone or hydroxyphenylacetic lactone. 2-Phenylcoumarone is also produced when hydroxydiphenylacetic lactone is heated with phosphorus tribromide at 200° in an oil-bath, whilst heating in a sealed tube yields 1-phenylcoumarone; 2-phenylcoumarone is also produced by heating the lactone with phosphorus pentasulphide at 210° .

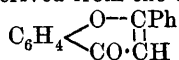
o-Anisylphenylethane [*o*-methoxy-*aa*-diphenylethane], $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CPhMe}$, prepared by reducing *o*-methoxydiphenylethylene with sodium and alcohol, is a colourless liquid of camphor-like odour, boils at $160\text{--}161^\circ$ under 11 mm. pressure, and solidifies to crystals melting at 26° . *o*-Hydroxy-*aa*-diphenylethane, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CPhMe}$, prepared by hydrolysing the ether with alcoholic potassium hydroxide at 200° , boils at $177\text{--}178^\circ$ under 12 mm. pressure, has a sp. gr. 1.0778 at 20° , and n_D 1.5868; the sodium derivative separates from the strongly alkaline solution, and can be extracted with ether; the phenylurethane crystallises from dilute alcohol or from light petroleum in white, glistening needles and melts at 99° .

p-Hydroxydibenzyl, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$, prepared by hydrolysing its methyl ether with alcoholic potash at 200° , crystallises from dilute alcohol in glistening flakes and melts at $100\text{--}101^\circ$; the phenylurethane crystallises from alcohol or light petroleum in glistening, white flakes and melts at 150° . The phenol obtained by Stoermer and Reuter (this vol., i, 181), by the action of hydrogen iodide on 2-phenylcoumaran, is isomeric with the two preceding phenols, but is not identical with either, and its nature is at present unknown; a hydrocarbon which was also produced in the same interaction has been identified as β -phenylnaphthalene; this hydrocarbon, which is also produced by the action of hydrogen iodide on phenoxystyrene, $\text{CHPh}\cdot\text{CH}\cdot\text{OPh}$, is probably formed by hydrolysis of the 2-phenylcoumaran, by addition of 2HI, to phenol and styrene di-iodide, $\text{C}_6\text{H}_5\cdot\text{CHI}\cdot\text{CH}_2\text{I}$, and condensation of two mols. of the di-iodide with elimination of 4HI to form phenylnaphthalene.

It was thought that *o*-hydroxydiphenylethylene might be reduced with hydrogen iodide to the *o*-hydroxydiphenylethane just described, just as styrene is reduced to ethylbenzene, but the actual product is the

para-compound (Koenigs and Carl, Abstr., 1892, 446), which is probably formed by reduction to styrene and phenol, as these condense to form the parahydroxy-compound, although the ortho-compound is also found in the condensation product; the *phenylurethane*, $C_{21}H_{19}O_2N$, of *p*-hydroxydiphenylethane crystallises from light petroleum in glistening, white needles and melts at 111° . T. M. L.

Syntheses of 3:4-Dihydroxyflavone. GERTRUD WOKER, STANISLAUS VON KOSTANECKI, and JOSEF TAMBOR (*Ber.*, 1903, **36**, 4235—4244).—The compounds prepared by Friedländer and Rüdelt by condensing α -chloro-*o*-hydroxyacetophenone with aromatic aldehydes, and formulated by them as flavones derived from the compound



(Abstr., 1896, i, 439), have been shown by Kostanecki and his pupils to be oxindogenide derivatives $C_6H_4 \begin{array}{c} \diagup O \\ \diagdown CO \end{array} C:CHPh$ (Abstr., 1896, i, 606); final proof of this view is afforded by the synthesis of 3:4-dihydroxyflavone, which has been found to be isomeric, and not identical with Friedländer's compound.

2'-Hydroxy-3':4'-dimethoxychalkone, $OH \cdot C_6H_2(OMe)_2 \cdot CO \cdot CH:CHPh$, prepared from gallacetophenone dimethyl ether and benzaldehyde, crystallises from dilute alcohol in long, golden-yellow needles, and melts at 98° . The *acetyl* derivative, $C_{19}H_{18}O_5$, crystallises from alcohol in long needles and melts at 110° ; its *dibromide*, $C_{19}H_{18}O_5Br_2$, crystallises from alcohol in white prisms and melts at 140° . *3':4'-Dimethoxy-*

flavone, $C_6H_2(OMe)_2 \begin{array}{c} \diagup O-CPh \\ \diagdown CO-CH \end{array}$, prepared by the action of alcoholic potassium hydroxide on the preceding compound, crystallises from alcohol in white needles, melts at 151° , and yields benzoic acid and gallacetophenone dimethyl ether, when boiled with sodium ethoxide.

3:4-Dihydroxyflavone, $C_6H_2(OH)_2 \begin{array}{c} \diagup O-CPh \\ \diagdown CO-CH \end{array}$, crystallises from 50 per cent. alcohol in very pale yellow needles and melts at 239° . The *acetyl* derivative, $C_{19}H_{14}O_6$, crystallises from alcohol in white needles and melts at 193° .

3:4-Dimethoxyflavanone, $C_6H_2(OMe)_2 \begin{array}{c} \diagup O-CHPh \\ \diagdown CO-CH_2 \end{array}$, prepared by the direct action of sodium hydroxide on an alcoholic solution of benzaldehyde and gallacetophenone dimethyl ether, crystallises from methyl alcohol in white needles and melts at 115° . The *bromo-derivative*, $C_{17}H_{15}BrO_4$, crystallises from alcohol in needles and melts at 110° ; when acted on by alcoholic potassium hydroxide, it also yields dihydroxyflavone, thus affording a second method of synthesis.

T. M. L.

Bromine Derivatives of the Cinchona Alkaloids and the corresponding Compounds containing less Hydrogen. A. CHRISTENSEN (*J. pr. Chem.*, 1903, [ii], **68**, 425—448. Compare Abstr., 1901, i, 481).—The dibromides of quinine, cinchonine, and cinchonidine are best prepared by adding bromine to the alkaloid in hydrogen

bromide and glacial acetic acid solution. From the hydrobromides so obtained, the dibromides are liberated on addition of aqueous sodium hydroxide. When acted on by alcoholic potassium hydroxide, these dibromides easily lose HBr, being converted into the monobromo-substitution derivatives of the alkaloids, which again lose HBr on prolonged boiling with alcoholic potassium hydroxide, and yield the dehydro-alkaloids (Koenigs and Comstock, *Abstr.*, 1892, 1010).

With bromine in aqueous solution, cinchonine dibromide hydrobromide forms the perbromide, which dissolves on boiling to a red solution with green fluorescence. On addition of more bromine and cooling, a substance is obtained as an orange-coloured precipitate. In alcoholic solution, the substance is red by transmitted, green by reflected light, the aqueous solution has a yellowish-green fluorescence, and gives a red to violet precipitate with ammonia. Similar results are obtained with cinchonidine dibromide.

Bromocinchonine, $C_{19}H_{21}ON_2Br$, crystallises in long needles or long, thin, rhombic plates, melts and becomes brown at $225-226^\circ$, and has $[\alpha]_D + 185.7^\circ$ at 17° . On treatment with zinc and dilute sulphuric acid, bromocinchonine gradually loses bromine. The *hydrochloride*, $C_{19}H_{21}ON_2Br \cdot HCl \cdot 2H_2O$, crystallises in long, thin leaflets; the *hydrobromide*, $C_{19}H_{21}ON_2Br \cdot 2HBr$, crystallises in rhombic plates and blackens and melts at 258° ; the *oxalate*, $(C_{19}H_{21}ON_2Br)_2 \cdot C_2H_2O_4 \cdot 7H_2O$, crystallises in quadratic needles, becomes anhydrous at 110° , and is only slightly soluble in water, but easily so in alcohol. The author has compared Koenig's and Comstock's dehydrocinchonine hydrobromide (*Abstr.*, 1887, 1123), and found it to be identical with bromocinchonine. A repetition of Laurent's work (*Compt. rend.*, 1849, 20, 312) shows his dibromocinchonine to be identical with cinchonine dibromide, and his sesquibromocinchonine to be a mixture of the dibromide with bromocinchonine.

Kopp's oxycinchonine, sesquioxycinchonine, and dioxycinchonine (*Arch. Pharm.*, 1876, 209, 34), obtained from Laurent's supposed three bromo-compounds, were most probably impure dehydrocinchonine. G. Y.

Corydalis Alkaloids. JOHANNES GADAMER (*Arch. Pharm.*, 1903, 241, 630—634).—An introduction to the following paper.

C. F. B.

Corybulbine and isoCorybulbine. DANIEL BRUNS (*Arch. Pharm.*, 1903, 241, 634—655. Compare *Abstr.*, 1901, i, 288; 1902, i, 306).—From 20 kilos. of *Corydalis cava* tubers, 5.75 per cent. of alkaloids was obtained, exclusive of corytuberine; only 0.185 per cent. of corybulbine was obtained in the impure state. It was purified by floating alcohol on a saturated (about 1 per cent.) solution of the alkaloid in chloroform; the melting point $237-238^\circ$ and composition $C_{21}H_{25}O_4N$ were confirmed; it has $[\alpha]_D + 303^\circ$, and is very sensitive to light. It is a monoacid base: the crystalline *hydrochloride* melts and decomposes at $245-250^\circ$; the *aurichloride* and *platinichloride* are amorphous, and could only be obtained of normal composition by adding a saturated

solution of the hydrochloride to excess of aqueous gold or platinum chloride.

Dehydrocorybulbine, $C_{21}H_{21}O_4N$, a monoacid base, melting at $210-211^\circ$, was obtained from the corybulbine by the action of iodine in alcoholic solution; the crystalline *hydrochloride* and *platinichloride* melt at $225-227^\circ$ and 236° respectively. If the iodide is mixed with 10 per cent. aqueous sodium hydroxide, the mixture warmed until the crystals which separate have redissolved, and the crystals which separate again on cooling recrystallised from water, *dehydrocorybulbine*, $C_{18}H_{12}(OMe)_3ON \cdot 5H_2O$, is obtained in dark reddish-violet needles which melt at $175-178^\circ$. Only $4H_2O$ are removed by drying over sulphuric acid; the 5th mol. is only removed by prolonged drying at 95° in a vacuum (heating in air brings about decomposition). Unlike berberine (Schmidt, Abstr., 1884, 339) and dehydrocorydaline (Ziegenbein, Abstr., 1897, i, 175), the substance has not the character of a ψ -ammonium base: it is not soluble in ether; it does not form compounds with chloroform, acetone, or ammonium sulphide, and it has no alkaline reaction. Evidently it is a phenolbetaine, water having been eliminated between the phenolic hydroxyl and that attached to the nitrogen atom.

If this view is correct, an acid derivative of dehydrocorybulbine, which would no longer contain the phenolic hydroxyl, should exhibit a different behaviour. An acetyl derivative could not be obtained, but *benzoyldehydrocorybulbine* was prepared by the Schotten-Baumann reaction. This melts at $173-174^\circ$, whilst its yellow *hydrochloride*, $C_{21}H_{20}BzO_4N \cdot HCl \cdot 2H_2O$, remains unmelted at 250° , and its yellow *nitrate* melts at $230-231^\circ$; it does form crystalline *additive compounds* with 1 mol. each of chloroform and acetone, melting at 176° and $201-202^\circ$ respectively, and with yellow ammonium sulphide.

Attempts to prepare an oxime from it were unsuccessful.

i-Corybulbine, obtained by the reduction of dehydrocorybulbine (Abstr., 1901, i, 288), forms a *hydrochloride*, also a *nitrate* melting at $207-208^\circ$; the *platinichloride* and the *aurichloride*, the latter melting at 223° , were obtained by filtering a solution of the hydrochloride into excess of aqueous platinum or gold chloride. An attempt to resolve the base into optically active isomerides by crystallisation of its bromocamphorsulphonate was unsuccessful.

*iso*Corybulbine, $C_{21}H_{25}O_4N$ (Gadamer and Ziegenbein, Abstr., 1902, i, 307), has $[\alpha]_D +299.8^\circ$; when heated for a day with iodine at $95-100^\circ$ in alcoholic solution, it is oxidised to *dehydroisocorybulbine*. The *hydriodide* of this base, $C_{21}H_{21}O_4N \cdot HI$, and the *nitrate* do not melt at 260° . The hydriodide yields a crystalline precipitate, presumably of the free base, when it is treated with aqueous sodium hydroxide; zinc and sulphuric acid reduce it to inactive *i*-isocorybulbine, which melts at $165-167^\circ$.

apo-Corydaline was prepared by boiling corydaline with hydriodic acid of sp. gr. 1.7 (Dobbie and Lauder, Trans., 1892, 609), and converted into the *hydrochloride*, $C_{18}H_{19}O_4N \cdot HCl$, which melts and decomposes at $220-222^\circ$; neither an aurichloride nor a platinichloride could be prepared, owing to the reducing action of the base. The same hydrochloride was obtained in a similar manner from corybulbine and *isocorybulbine*. Hence these substances must be regarded as isomerides

with the formula $C_{18}H_{15}N(OMe)_3 \cdot OH$, differing only in the positions of the OMe and OH groups, whilst corydaline must be regarded as $C_{18}H_{15}N(OMe)_4$, the group $C_{18}H_{15}N$ being the same in all three substances.

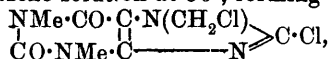
It is possible that *isocorybulbine* is not contained in the tubers, but is formed from corydaline during the working up of the tubers, when the solution of the uncrystallisable bases in light petroleum is treated with gaseous hydrogen chloride. C. F. B.

Cotarnine. IV. Application of Grignard's Reaction. MARTIN FREUND (*Ber.*, 1903, 36, 4257—4259. Compare Abstr., 1902, i, 556; 1903, i, 572).—*α-Methylhydrocotarnine*, prepared by the action of magnesium methiodide, was obtained as a viscous liquid. The *hydriodide*, $C_{13}H_{17}NO_3 \cdot HI$, crystallises from hot water in needles and melts at 178—180°. The *hydrobromide*, $C_{13}H_{17}NO_3 \cdot HBr$, crystallises in needles and melts at 199—200°. The *hydrogen sulphate*, $C_{13}H_{17}NO_3 \cdot H_2SO_4$, crystallises in needles and melts at 155°. The *platinichloride*, $(C_{13}H_{17}NO_3)_2 \cdot H_2PtCl_6$, crystallises from alcohol and melts at 220°. The *methiodide*, $C_{13}H_{17}NO_3 \cdot MeI$, separates from hot water in long, glistening crystals and melts at 228—229°. T. M. L.

Sparteine Sulphate. CHARLES MOUREU and AMAND VALEUR (*J. Pharm. Chim.*, 1903, [vi], 18, 545—546).—The salt has the formula $C_{15}H_{26}N_2 \cdot H_2SO_4 \cdot 5H_2O$. In aqueous solution at temperatures of 15° to 20°, it has $[\alpha]_D - 22 \cdot 12^\circ$. Only four of the molecules of water can be removed by desiccation over sulphuric acid under a reduced pressure in the cold. When heated to 100°, some decomposition of the sparteine takes place. A solution of the salt in water reacts acid to phenolphthalein, and the solution only becomes neutral when sufficient sodium hydroxide solution has been added to combine with one-half the sulphuric acid present in the salt (compare Abstr., 1903, i, 717). W. P. S.

Methyl and Ethyl Bromides of Alkaloids of the Tropeine and Scopoieine Groups. EMANUEL MERCK (D.R.-P. 145996).—The alkaloids of the tropeine and scopoieine groups combine with alkyl bromides when dissolved in alcohol or chloroform, yielding well-crystallised derivatives. *Hyoscyamine methobromide* forms colourless crystals melting at 210—212° and dissolving readily in water, sparingly in cold alcohol, insoluble in ether. *Atropine methobromide* crystallises from alcohol in white, glistening scales and melts at 222—223°; the *ethyl* compound dissolves in alcohol or water and melts at 173—174°. *Homatropine methobromide* forms colourless crystals and melts at 180—181°. *Scopolamine methobromide* crystallises from ether-alcohol in white needles and melts and decomposes at 216—217°. C. H. D.

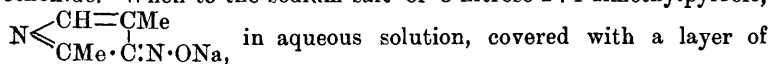
Preparation of Chlorotheophylline. C. F. BOEHRINGER & SÖHNE (D.R.-P. 145880).—Chlorocaffeine reacts with phosphorus pentachloride dissolved in phosphorus oxychloride at 100°, or with chlorine in nitrobenzene solution at 50°, forming 1':2-dichlorocaffeine,



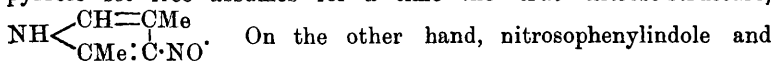
which crystallises from methyl alcohol in groups of long needles and melts at 145°. Warming with water or dilute acids or alkalis hydrolyses it to formaldehyde, hydrogen chloride, and 2-chloro-4:6-dimethylxanthine (chlorotheophylline, compare E. Fischer, Abstr., 1895, i, 12), which yields theophylline on reduction. C. H. D.

Transformation of 2-Methylpyrrolidine into 2-Methylpyrrole. GIUSEPPE TESTONI and LUIGI MASCARELLI (*Gazzetta*, 1903, 33, 267—269).—When 2-methylpyrrolidine is distilled over heated zinc dust, it is converted into 2-methylpyrrole; the latter was identified by its acetyl and cinnamyl derivatives. W. A. D.

Pyrrole Derivatives. ANGELO ANGELI, FRANCESCO ANGELICO, and ENRICO CALVELLO (*Gazzetta*, 1903, 33, 270—272. Compare Abstr., 1901, i, 747; ii, 381).—The sodium salts of nitroso-derivatives of indoles and pyrroles with an alkyl group in position 2 but with position 3 open, are readily obtained by the action of amyl nitrite and sodium ethoxide. When to the sodium salt of 3-nitroso-2:4-dimethylpyrrole,

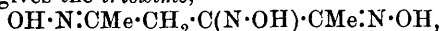


ether, dilute sulphuric acid is added, the ether becomes coloured with a beautiful but fugitive green tinge, showing that the nitroso-pyrrole set free assumes for a time the true nitroso-structure,



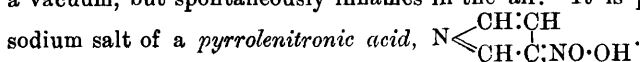
On the other hand, nitrosophenylindole and nitrosotriphenylpyrrole set free from their salts by carbonic or acetic acid are coloured yellow.

Nitrosoindoles are not acted on by hydroxylamine, but nitrosopyrroles are decomposed; thus the sodium salt of 3-nitroso-2:5-dimethylpyrrole gives the *trioxime*,



which yields a tribenzoyl derivative.

Another difference between nitrosoindoles and nitrosopyrroles is that the former on oxidation readily give nitro-compounds, but the latter undergo a complex change. Pyrrole, however, interacts with ethyl nitrate in presence of sodium forming a yellowish-brown crystalline powder, which dissolves in water and gives precipitates with salts of the heavy metals; this powder, when dried, is stable in a vacuum, but spontaneously inflames in the air. It is probably the



W. A. D.

Action of Bromosuccinic and Dibromosuccinic Acids on the Pyridine and Quinoline Bases. LOUIS DUBREUIL (*Compt. rend.*, 1903, 137, 1063—1065).—Bromosuccinic acid reacts with pyridine, quinoline, and quinaldine in alcoholic solution to form *pyridine hydrogen fumarate* melting at 193°, *quinoline hydrogen fumarate* melting at 153°, and *quinaldine fumarate* melting at 104° respectively. All these salts crystallise in white needles. In aqueous solution, pyridine gives pyridine hydrogen fumarate; quinoline yields *quinoline hydrogen malate* melting at 151°; whilst quinaldine unites directly with the acid forming *quinaldine bromosuccinate* melting at 57°, which is a very unstable salt breaking down into a mixture of quinaldine fumarate and bromide by merely dissolving in warm alcohol. Dibromosuccinic acid in alcoholic solution gives *pyridine hydrogen dibromosuccinate* melting at 137° with pyridine, *quinoline dibromosuccinate* melting at 108° with quinoline, and *quinaldine hydrogen dibromosuccinate* melting at 133° with quinaldine. The nature of the salt formed is independent of the relative proportions of the acid and base employed.

In aqueous solution, pyridine reacts with dibromosuccinic acid to form (1) *pyridine hydrogen bromofumarate* decomposing at 200°, (2) *pyridine hydrogen acetylenedicarboxylate* decomposing at 210°; quinoline gives under the same conditions *quinoline hydrogen acetylenedicarboxylate* decomposing at 210°, whilst quinaldine yields *quinaldine hydrogen bromomaleate* melting at 130°.

M. A. W.

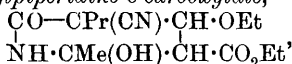
The Piperidylcarbamides. BOUCHETAL DE LA ROCHE (*Bull. Soc. chim.*, 1904, [iii], 31, 21—24).—The piperidylcarbamides can be obtained by heating piperidine with carbamide or its substitution products. Piperidylcarbamide melts at 93°; *m-chlorophenylpiperidylcarbamide* forms colourless plates melting at 149·5°, soluble in alcohol, ether, or chloroform, sparingly so in benzene; *p-chlorophenylpiperidylcarbamide* forms colourless needles melting at 173—174°, soluble in hot alcohol, chloroform, acetic acid; *m-bromophenylpiperidylcarbamide* forms colourless plates which melt at 157°; *p-bromophenylpiperidylcarbamide* melts at 188°; 1:2:5-nitrotolylpiperidylcarbamide forms small, pale yellow needles melting at 152°. Chlorine and bromine act on phenylpiperidylcarbamide giving *trichlorophenylpiperidylcarbamide*, which volatilises at 275—280° without melting, and *tribromophenylpiperidylcarbamide*, which sublimates about 260°. Sulphuric acid attacks these symmetrical carbamides with evolution of carbon dioxide, giving a sulphonated amine; the action of nitric acid is similar. Reducing agents do not attack a piperidylcarbamide unless it contains a nitro-group, whilst boiling alcoholic or aqueous alkali hydroxides are without action.

S. S.

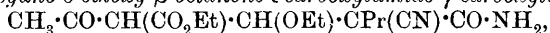
Action of Ethyl Ethoxymethyleneacetoacetate on Monoalkylcyanoacetamides. GIORGIO ERRERA and L. LABATE (*Gazzetta*, 1903, 33, ii, 161—170).—The compound previously obtained by Errera (*Abstr.*, 1902, i, 117) by the interaction of ethyl α -ethoxymethyleneacetoacetate and methylcyanoacetamide, and then described as ethyl ϵ -cyano- δ -ethoxy- β -hexanone- ϵ -carboxylamide- γ -carboxylate, is

probably *ethyl 5-cyano-2-hydroxy-4-ethoxy-6-keto-2:5-dimethylpyridine-3-carboxylate*, $\text{CO}\cdot\text{CMe}(\text{CN})\cdot\overset{\text{OEt}}{\underset{\text{NH}\cdot\text{CMe}(\text{OH})\cdot\text{CH}\cdot\text{CO}_2\text{Et}}{\text{CH}}}$ for it reacts neither with hydroxylamine nor phenylhydrazine, and its methyl derivative, when treated with concentrated hydrochloric acid, yields 6-hydroxy-2:5-dimethylpyridine-3-carboxylic acid.

The interaction of propylcyanoacetamide, sodium ethoxide, and ethyl ethoxymethyleneacetoacetate yields *ethyl 5-cyano-2-hydroxy-4-ethoxy-6-keto-2-methyl-5-propylpyridine-6-carboxylate*,



or *ethyl ε-cyano-δ-ethoxy-β-octanone-ε-carboxylamide-γ-carboxylate*,



which crystallises from aqueous alcohol in silvery plates melting at 260°. On boiling with hydrochloric acid, it yields *ethyl 6-hydroxy-5-propyl-2-methylpyridine-3-carboxylate*, $\text{C}_{12}\text{H}_{17}\text{O}_3\text{N}$, which crystallises from alcohol in shining needles melting at 152°. *6-Hydroxy-5-propyl-2-methylpyridine-3-carboxylic acid*, $\text{C}_{10}\text{H}_{13}\text{O}_3\text{N}$, is deposited from alcohol in slender needles melting and decomposing at about 300°.

Ethyl 5-cyano-2-hydroxy-4-ethoxy-6-keto-2-methyl-5-ethylpyridine-3-carboxylate or *ethyl ε-cyano-δ-ethoxy-β-heptanone-ε-carboxylamido-γ-carboxylate*, $\text{C}_{14}\text{H}_{22}\text{O}_5\text{N}_2$, prepared from ethylcyanoacetamide, crystallises in colourless needles melting at 198°.

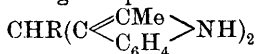
Ethyl 6-hydroxy-5-ethyl-2-methylpyridine-3-carboxylate, $\text{C}_{11}\text{H}_{15}\text{O}_3\text{N}$, crystallises from alcohol in short needles melting at 190°, and the corresponding *acid*, $\text{C}_9\text{H}_{11}\text{O}_3\text{N}$, in needles melting and decomposing at 305°.

Ethyl 6-methoxy-2:5-dimethylpyridine-3-carboxylate, $\text{C}_{11}\text{H}_{15}\text{O}_3\text{N}$, is deposited from aqueous solution in white needles or from benzine in silky needles containing H_2O , which is lost at 70°, the anhydrous compound then melting at 80°; it is readily soluble in methyl or ethyl alcohol.

6-Methoxy-2:5-dimethylpyridine-3-carboxylic acid, $\text{C}_9\text{H}_{12}\text{O}_3\text{N}$, crystallises from alcohol or benzine in needles melting at 167–168°.

T. H. P.

2-Methylindole. CARL RENZ and K. LOEW (*Ber.*, 1903, 36, 4326–4330).—The following compounds of the type



were prepared by condensing 2-methylindole with various aldehydes; the figures in brackets denote the temperature and time of condensation.

The *compound*, $\text{C}_{21}\text{H}_{22}\text{N}_2$, from propaldehyde (100°, 5 hours) crystallises from alcohol in lustrous prisms and melts at 180°. That from *isobutaldehyde*, $\text{C}_{22}\text{H}_{24}\text{N}_2$ (100°, 6 hours), separates from acetone in prismatic plates and melts at 207°. The *derivative*, $\text{C}_{23}\text{H}_{20}\text{ON}_2$, from *furfuraldehyde* (100°, 6 hours), forms small prisms melting at 220°. From *tolualdehyde* (120–130°, 6 hours), the *compound* $\text{C}_{26}\text{H}_{24}\text{N}_2$ is obtained; it crystallises from alcohol in tetragonal prisms and melts

at 217—218°. From *o*- and *p*-nitrobenzaldehydes (130—140°, 5 hours), isomeric compounds, $C_{25}H_{21}O_2N_3$, are obtained, melting respectively at 230° and 233°. With salicylaldehyde (130—140°, 5 hours), 2-methylindole gives the compound $C_{25}H_{22}ON_3$, which crystallises from acetone in white plates and melts at 230—231°. Anisaldehyde (120—130°, 5 hours) gives the substance $C_{26}H_{24}ON_2$, forms white needles, and melts at 211—212°; whilst from cinnamaldehyde (110°, 6 hours) the crystalline compound, $C_{27}H_{24}N_2$, is obtained, melting at 206°. Cuminaldehyde gives the derivative $C_{28}H_{28}N_2$, which separates from alcohol in large, white crystals and melts at 218—219°, and piperonal the compound $C_{26}H_{22}O_2N_2$, crystallising from aqueous acetone in leaflets and melting at 213°.

W. A. D.

Derivatives of 7-Hydroxyquinoline. CARL BÜLOW and GOTTHOLD ISSLER (*Ber.*, 1903, 36, 4013—4019. Compare Abstr., 1903, i, 718).—*Acetylacetone-m-hydroxyanilide*, $OH \cdot C_6H_4 \cdot N : CMe \cdot CH : CMe \cdot OH$, crystallises from alcohol in colourless flakes, melts at 135°, and is hydrolysed by alkalis into *m*-aminophenol, acetone, and acetic acid. By the action of hydrogen chloride on a solution of the anilide in acetic acid, it is converted into 7-hydroxy-2 : 4-dimethylquinoline, $C_{11}H_{11}ON$, which crystallises from alcohol in white needles and melts at 218°; the *hydrochloride* crystallises from alcoholic hydrochloric acid in orange-coloured needles.

Dibenzoylmethane-m-hydroxyanilide, $OH \cdot C_6H_4 \cdot N : CPh \cdot CH : CPh \cdot OH$, crystallises from alcohol in yellow needles and melts at 172°.

7-Hydroxy-2 : 4-diphenylquinoline, $C_{21}H_{15}ON$, crystallises from alcohol in long, white, silky, felted needles, and melts at 272°.

Propionylacetophenone-m-hydroxyanilide,

$OH \cdot C_6H_4 \cdot N : CEt \cdot CH : CPh \cdot OH$, crystallises from alcohol in yellow prisms and melts at 139°.

7-Hydroxy-4-phenyl-2-ethylquinoline, $C_{17}H_{15}ON$, crystallises from alcohol in yellow needles and melts at 251°.

Butyrylacetophenone-m-hydroxyanilide,

$HO \cdot C_6H_4 \cdot N : CPr^a \cdot CH : CPh \cdot OH$, crystallises from alcohol in yellow, rhombic tablets and melts at 152°. 7-Hydroxy-4-phenyl-2-propylquinoline, $C_{18}H_{17}ON$, crystallises from alcohol in minute, white needles and melts at 221°.

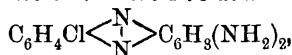
T. M. L.

Condensations of Cinnamaldehyde and Protocatechualdehyde. CARL RENZ and K. LOEW (*Ber.*, 1903, 36, 4330—4332).—When molecular quantities of cinnamaldehyde and quinaldine are heated for 6 hours at 150°, the compound, $C_{19}H_{15}N$, is formed by elimination of $1H_2O$; it crystallises from alcohol in lustrous, prismatic, bright yellow leaflets and melts at 117°. The similar compound, $C_{17}H_{13}O_2N$, prepared from protocatechualdehyde and quinaldine crystallises from alcohol, melts at 249°, and gives a *hydrochloride*, $C_{17}H_{13}O_2N \cdot HCl \cdot H_2O$, which forms felted, reddish-yellow needles and melts at 295°. The compound formed by condensing protocatechualdehyde and lepidine was isolated as the crystalline *hydrochloride*, $C_{17}H_{13}O_2N \cdot HCl$, which sinters at 234° and melts at 245°; the *platinichloride* darkens at 210° and melts at 215°.

W. A. D.

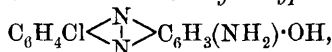
Oxidation of Substituted *o*-Phenylenediamines. FRITZ ULLMANN and FERD. MAUTNER (*Ber.*, 1903, **36**, 4026—4034. Compare Abstr., 1903, i, 199) — The preparation of phenazine derivatives by oxidation of *o*-phenylenediamine may be extended to substituted *o*-diamines. 4-Chloro-*o*-phenylenediamine is best prepared by nitrating *p*-chloroacetanilide and reducing the nitro-compound with stannous chloride. As the base has been little investigated, some derivatives were prepared. The *sulphate* forms colourless leaflets, dissolving sparingly in cold, readily in hot water or alcohol. 4-Chloro-1:2-di-acetylaminobenzene crystallises from toluene in colourless leaflets and melts and decomposes at about 201°, forming 4-chloromethylbenzimidazole, $C_8H_7N_2Cl$, leaflets melting at 199° and dissolving readily in alcohol or ether, sparingly in benzene. Nitrous acid converts the diamine into 4-chloroazaminobenzene, $C_6H_4N_3Cl$, which separates from xylene in colourless crystals and melts at 156°, dissolving readily in alcohol or ether, less readily in toluene. Chlorophenylenediamine combines with phenanthraquinone in acetic acid solution, forming phenanthrachlorophenazine, $C_{20}H_{11}N_2Cl$, crystallising from nitrobenzene in greenish-yellow leaflets and melting at 246°, almost insoluble in alcohol and ether, dissolving in concentrated sulphuric acid to a red solution.

Ferric chloride in acetic acid solution oxidises the chlorodiamine at the ordinary temperature to 7-chloro-2:3-diaminophenazine,



which crystallises from boiling aniline in yellowish-brown needles, does not melt at 360°, and dissolves in glacial acetic acid to a red solution. The *hydrochloride* and *nitrate* form brown needles and show a slight green fluorescence in alcoholic solution.

When the oxidation is performed in hydrochloric acid solution, the principal product is 7-chloro-2-amino-3-hydroxyphenazine,



separating from boiling alcohol, in which it is very sparingly soluble, in small, yellow needles, and dissolving in alkalis to yellow solutions. The *hydrochloride* and *nitrate* form brown needles.

Both phenazines combine with *o*-phenylenediamine hydrochloride on heating in fused benzoic acid at 250° to form 2-chlorohomofluorindine, $C_{18}H_{11}N_4Cl$, crystallising from nitrobenzene in greenish-blue needles and dissolving in alcohol to a violet solution with red fluorescence, and in sulphuric acid to a blue solution. The *hydrochloride* forms blue needles, insoluble in water, sparingly soluble in alcohol.

7-Chloro-2-amino-3-hydroxyphenazine combines with chloro-*o*-phenylenediamine to form 2:10-dichlorohomofluorindine, $C_{18}H_{10}N_4Cl_2$, the solutions of which are greener in shade than those of the monochloro-compound.

Ferric chloride oxidises 4-bromo-*o*-phenylenediamine to 7-bromo-2:3-diaminophenazine and 7-bromo-2-amino-3-hydroxyphenazine, which resemble the corresponding chloro-compounds.

3:4-Diaminobenzoic acid, prepared from 3-nitro-*p*-acetotoluide by

oxidation with calcium permanganate, hydrolysis, and reduction with sodium hydroxide and aluminium, is oxidised by ferric chloride, forming brown crystals of 2-amino-3-hydroxyphenazinecarboxylic acid, dissolving in alkalis to yellowish-red solutions. The carboxyl group is not eliminated on heating. *o*-Phenylenediamine hydrochloride in presence of benzoic acid forms *homofluorindine-2-carboxylic acid*, $C_{19}H_{13}O_2N_4$, blue crystals, dissolving in dilute alkali hydroxides to reddish-violet solutions, and in concentrated sulphuric acid to a cornflower-blue solution. The same acid is obtained on heating 2:3-diaminophenazine with 3:4-diaminobenzoic acid and benzoic acid at 240—250°.

o-Phenylenediamine-4-sulphonic acid could not be oxidised to an azine derivative, but reacts when its hydrochloride is heated with 2:3-diaminophenazine and water at 150—160°, forming blue crystals with bronze lustre of *homofluorindine-2-sulphonic acid*, dissolving in ammonia to a red solution, appearing violet in a thin layer.

C. H. D.

Transformation of Benzidine. ARNOLD F. HOLLEMAN and J. POTTER VAN LOON (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 262—267. Compare Abstr., 1903, i, 249).—Hydrazobenzene was separated as a snow-white substance which turns faintly yellow on exposure to air. The respective influences of the concentration of the acid, the solvent, the particular acid used, and the temperature, on the transformation of hydrazobenzene into benzidine have been studied.

The velocity of the transformation is expressed by the equation $dC_b/dt = KC^2_{HCl}$, where C_b is the concentration of the benzidine formed, C_{HCl} the concentration of the hydrochloric acid at any moment, t the time in minutes, and K the reaction constant.

A. McK.

Reduction of 2-Nitronaphthalene. JAKOB MEISENHEIMER and KLAUS WITTE (*Ber.*, 1903, 36, 4153—4164).—A 30—35 per cent. yield of 2-nitronaphthalene may be obtained from β -naphthylamine by Sandmeyer's method (Abstr., 1887, 720) if a larger excess of acid is used during the process of diazotising, and if the mixture is left for a longer time in contact with the cuprous oxide mixture. When an alcoholic solution of the nitro-compound is boiled with aqueous sodium hydroxide and zinc dust and then air drawn through the solution, a mixture of 2:2-azonaphthalene melting at 208° (compare Hantzsch and Schmiedel, Abstr., 1897, i, 185), 2:2-diamino-1:1-dinaphthyl, 1:1-dinaphtha-2:2-*o*-diazine, and β -naphthylamine is obtained. The mixture is treated with concentrated hydrochloric acid, when the azo-compound remains undissolved; on the addition of water to the filtrate, the diazine is precipitated, and the addition of ammonia to the second filtrate yields the diaminodinaphthyl.

When 2:2-azonaphthalene is reduced by boiling for 2 to 3 minutes with alcohol, sodium hydroxide, and zinc dust, the chief product is 2:2-hydrazonaphthalene, $C_{10}H_7 \cdot NH \cdot NH \cdot C_{10}H_7$, which crystallises in faintly red plates melting at 140—141°. It dissolves readily in most

organic solvents, and the solutions in contact with atmospheric oxygen readily yield azonaphthalene.

Mineral acids readily transform the hydrazo-compound into the isomeric 2:2-diamino-1:1-dinaphthyl, $\text{NH}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{C}_{10}\text{H}_6 \cdot \text{NH}_2$; prolonged boiling with alkalis also produces the same transformation, and the same compound is formed when azonaphthalene is reduced with zinc dust and acetic acid. It crystallises in colourless needles, melts at 191° , and is readily soluble in most organic solvents, but only sparingly so in methyl or ethyl alcohol. The *hydrochloride*, $\text{C}_{20}\text{H}_{16}\text{N}_2 \cdot 2\text{HCl}$, forms long, colourless needles which, when heated at $240\text{--}250^\circ$ for 5 minutes, yields 1:1-dinaphtho-2:2-imine (Walder, Abstr., 1883, 208).

1:1-Dinaphtha-2:2-o-diazine, $\begin{matrix} \text{C}_{10}\text{H}_6 \cdot \text{N} \\ | \\ \text{C}_{10}\text{H}_6 \cdot \text{N} \end{matrix}$, crystallises from alcohol in large, hard needles melting at $267\text{--}268^\circ$, is only sparingly soluble in the usual organic solvents, but dissolves readily in concentrated hydrochloric acid. The *hydrochloride* forms red needles which gradually lose hydrogen chloride; the *platinichloride*, $(\text{C}_{20}\text{H}_{12}\text{N}_2)_2 \cdot \text{H}_2\text{PtCl}_6$, forms yellowish-red needles. The diazine is not readily reduced by zinc dust and alkali or by stannous chloride, but with zinc dust and acetic acid yields 2:2-diamino-1:1-dinaphthyl.

When 2-nitronaphthalene is reduced with sodium stannite solution, it yields 2:2-azoxynaphthalene and 1:1-dinaphtha-2:2-o-diazine oxide. 2:2-Azoxynaphthalene, $\text{ON}_2(\text{C}_{10}\text{H}_7)_2$, is soluble in ether and crystallises in small, yellow needles melting at $167\text{--}168^\circ$ to a deep red liquid; on reduction with zinc dust and alkali, it yields azonaphthalene.

1:1-Dinaphtha-2:2-o-diazine oxide, $\text{O} < \begin{matrix} \text{N} \cdot \text{C}_{10}\text{H}_6 \\ | \\ \text{N} \cdot \text{C}_{10}\text{H}_6 \end{matrix}$, is insoluble in ether, crystallises in pale yellow needles, melts and decomposes at $247\text{--}248^\circ$, is sparingly soluble in most solvents, and on reduction yields dinaphtha-diazine. J. J. S.

Decomposition of Phenylhydrazones. II. OTTO ANSELMINO (*Ber.*, 1903, 36, 3974—3975. Compare Abstr., 1903, i, 367).—*p*-Hydroxybenzaldehydephenylhydrazone, unlike the ortho-compound, does not yield *p*-cyanophenol and aniline when heated; the distillate contains only a small amount of aniline and none of the cyanophenol. The acetylphenylhydrazone gives acetanilide, but the second product could not be isolated. The diacetylphenylhydrazone, however, gives acetanilide and the acetylated cyanophenol melting at 57° .

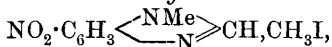
p-Hydroxybenzaldehydeacetylphenylhydrazone, crystallises from alcohol in short needles and melts at 182° . The *diacetyl* compound crystallises from a mixture of light petroleum and benzene and melts at 148° . T. M. L.

Lactose Phenyllosazone. CHARLES PORCHER (*Bull. Soc. chim.*, 1903, [iii], 29, 1225—1227. Compare Fischer, Abstr., 1885, 53).—The phenyllosazone of lactose is unstable and loses water even when dried at atmospheric temperatures, forming an anhydride, which is sparingly soluble in acetone and melts at $223\text{--}224^\circ$. This change, it

is suggested, accounts for the variety of melting points ascribed to lactose phenylosazone, since the latter becomes more or less dehydrated according to the rate and method of heating adopted in determining this constant. T. A. H.

Preparation of 4:5-Diamino-2:6-dihydroxypyrimidine. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 144761).—Diacetylaminouracil (diacetylaminodihydroxypyrimidine) is hydrolysed by gentle boiling with a concentrated solution of sodium hydroxide. Both acetyl groups are removed, forming 4:5-diamino-2:6-dihydroxypyrimidine, $\text{NH}\cdot\text{CO}\cdot\text{C}\cdot\text{NH}_2$, which may be isolated in the form of its sparingly soluble *sulphate*, $\text{C}_4\text{H}_6\text{O}_2\text{N}_4\cdot\text{H}_2\text{SO}_4\cdot 1\frac{1}{2}\text{H}_2\text{O}$. The formyl derivative (Traube, Abstr., 1900, i, 416) is not hydrolysable by this process, inasmuch as the ring closes forming xanthine. C. H. D.

Benziminazoles. OTTO FISCHER and WALTER HESS (*Ber.*, 1903, 36, 3967—3974).—6-Nitro-1-methylbenziminazole *methiodide*,



crystallises from methyl alcohol in yellow prisms and melts at 259°. The *periodide*, $\text{C}_9\text{H}_{10}\text{O}_2\text{N}_3\text{I}_3$, forms dark brown crystals. Alkalis convert the *methiodide* into 6-nitro-1:3-dimethylbenziminazolol, $\text{NO}_2\cdot\text{C}_6\text{H}_3\left\langle\begin{array}{c}\text{NMe} \\ \text{NMe} \end{array}\right\rangle\text{CH}\cdot\text{OH}$, which crystallises from dilute alcohol in yellow flakes, melts at 128°, is hydrolysed to formic acid and *m*-nitro-*o*-phenyldimethyldiamine, and can be prepared by heating the latter with glacial formic acid. When the diamine is heated with acetic acid and acetic anhydride it yields 6-nitro-1:2:3-trimethylbenziminazolol, $\text{NO}_2\cdot\text{C}_6\text{H}_3\left\langle\begin{array}{c}\text{NMe} \\ \text{NMe} \end{array}\right\rangle\text{CMe}\cdot\text{OH}$, which crystallises from dilute alcohol in yellow flakes, melts at 175°, and is hydrolysed to the diamine and acetic acid, though not so readily as the unmethylated compound. The corresponding *iminoazole* separates from hot water in white needles; the *methiodide*, $\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_3\text{I}$, separates from dilute methyl alcohol in yellow needles and melts at 267°; the *periodide*, $\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_3\text{I}_3$, forms brown needles.

Nitromethylbenziminazole, $\text{C}_8\text{H}_7\text{O}_2\text{N}_3$, prepared by nitrating the methylbenziminazole from 1:3:4-toluylenediamine and formic acid, crystallises from hot benzene in flat tablets and melts at 241°. The *methiodide*, $\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_3\text{I}$, of the methylated base crystallises from water in yellow flakes and melts at 238°; the brown *periodide*, $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_3\text{I}_3$, was crystallised from hot methyl alcohol. *Nitro-1:3:5-trimethylbenziminazolol*, $\text{C}_{10}\text{H}_{13}\text{O}_3\text{N}_3$, crystallises from dilute alcohol in yellow needles and melts and decomposes at 150°. When hydrolysed, it yields a *nitrotolylenedimethyldiamine*, $\text{C}_9\text{H}_{13}\text{O}_2\text{N}_3$, which crystallises from dilute alcohol in scarlet prisms and melts at 194°. The *methiodide* of nitro-1:2:5-trimethylbenziminazole, $\text{C}_{11}\text{H}_{14}\text{O}_2\text{N}_3\text{I}$, separates from water in colourless needles and melts at 297°; the *periodide*, $\text{C}_{11}\text{H}_{14}\text{O}_2\text{N}_3\text{I}_3$, forms long, brownish-red prisms; the *iminazolol*

(carbinol), prepared from the methiodide, crystallises from dilute alcohol in yellow tablets and melts at 195° .

Nitro-4 : 6-dimethylbenziminazole, $C_9H_9O_2N_3$, prepared by nitrating 4 : 6-dimethylbenziminazole, separates from alcohol in white prisms and melts at 268° . On methylation, it gives the *methiodide*, $C_{11}H_{14}O_2N_3I$, which crystallises from alcohol in colourless needles and melts at 214° ; the *periodide*, $C_{11}H_{14}O_2N_3I_3$, is also produced. The *carbinol*, $C_{11}H_{15}O_2N_3$, from the methiodide, crystallises from alcohol in glistening, orange-red prisms, melts at 163° , and is not hydrolysed by alkalis, although there is produced a certain amount of *nitroxylenyldimethylcarbamide*, $C_{11}H_{13}O_3N_3$, which crystallises from dilute alcohol in lemon-yellow needles and melts at 132° .

T. M. L.

Preparation of Alkylated 4-Amino-1-phenyl-2 : 3-dimethyl-5-pyrazolones. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 145603).—4-Bromo-1-phenyl-2 : 3-dimethyl-5-pyrazolone reacts with secondary amines, the bromine atom being replaced by the NR_2 group. The chloro- and iodo-derivatives react differently, the halogen atom being replaced by hydrogen.

Dimethylamine reacts in aqueous solution at 150° in a closed vessel, forming the 4-dimethylamino-derivative. Methylethylamine forms 4-methylethylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone, which crystallises from water in leaflets melting at 92° , dissolving easily in alcohol or ether, less readily in water or light petroleum. 4-Piperidino-1-phenyl-2 : 3-dimethyl-5-pyrazolone crystallises from alcohol in needles and melts at 145° .

C. H. D.

Constitution of Rosaniline and Pararosaniline. WALTER L. JENNINGS (*Ber.*, 1903, **36**, 4022—4026. Compare Baeyer and Villiger, *Abstr.*, 1903, i, 811).—Several authors have obtained an amorphous, red precipitate by the addition of sodium hydroxide to a cooled solution of magenta, giving figures on analysis lying between those required by the carbinol and by the anhydride formula.

Anhydro-p-triaminodiphenyltolylcarbinol, $C_{20}H_{19}N_3$, prepared by heating rosaniline, previously purified by crystallisation from boiling sodium hydroxide solution, at 200° for 2 hours in a current of dry hydrogen, forms a dark red, amorphous mass, insoluble in water and most organic solvents, but dissolving readily in acetone and rather less readily in methyl alcohol. Hydrochloric acid reconverts it into rosaniline hydrochloride.

Anhydro-p-triaminotriphenylcarbinol, $C_{19}H_{17}N_3$, prepared in the same manner from pararosaniline, is also amorphous, and is converted into pararosaniline hydrochloride by hydrochloric acid. The formation of these anhydrides confirms the quinonoid character of magenta and paramagenta.

C. H. D.

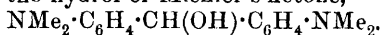
Preparation of Triphenylmethane Dyes from Magnesium Dimethylaminophenyl Bromide as a Lecture Experiment. PAUL EHRLICH and FRANZ SACHS (*Ber.*, 1903, **36**, 4296—4299).—No action occurs when magnesium is added to a solution of bromodimethylaniline in absolute ether. The Grignard reaction does, however, take place under the following conditions. Magnesium

powder is covered with absolute ether and ethyl bromide then added. After the ensuing vigorous action is moderated by cooling the mixture, the liquid is decanted and an ethereal solution of bromodimethylaniline added to the magnesium, which is apparently rendered active in this manner so that action ensues with the formation of magnesium dimethylaminophenyl bromide. The latter then reacts with Michler's ketone to give a blue product, which, when acidified by acetic acid, gives hexamethyltriaminotriphenylcarbinol, a product identical with methyl violet.

When benzophenone is used instead of Michler's ketone, dimethylaminotriphenylcarbinol is formed. When an ester of an aromatic carboxylic acid, such as ethyl benzoate, is used, malachite-green or an homologue is produced.

The successive introduction of dimethylamino-groupings into the molecule of triphenylcarbinol may easily be illustrated as a lecture experiment.

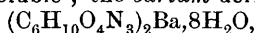
Magnesium dimethylaminophenyl bromide interacts with dimethylaminobenzaldehyde to form a product which, on acidification by acetic acid, yields the hydrol of Michler's ketone,



A. McK.

Formation of Reduced Osotriazoles. HANS EULER and ASTRID EULER (*Ber.*, 1903, **36**, 4253—4256).—*Ethyl 1:2-dihydroxy-triazolidine-4-acetate*, $\begin{matrix} \text{OH} \cdot \text{N} \cdot \text{CH}_2 \\ \text{OH} \cdot \text{N} \cdot \text{NH} \end{matrix} > \text{C} : \text{CH} \cdot \text{CO}_2\text{Et}$, prepared by reducing

the ammonium derivative of ethyl γ -isonitroso- β -nitrosoamino-crotonate (this vol., i, 146) by means of zinc and acetic acid, crystallises in colourless prisms, melts at 70—71°, and is an acid of similar strength to *o*-nitrobenzoic acid; the *potassium* derivative is colourless and readily soluble; the *barium* derivative,



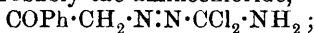
forms soluble, silky needles; the *silver* derivative, $\text{C}_6\text{H}_{10}\text{O}_4\text{N}_3\text{Ag}$, can be crystallised from alcohol; the *cupric* and *ferric* derivatives were also prepared.

1-Hydroxytriazoline-4-acetic acid, $\begin{matrix} \text{HO} \cdot \text{N} \cdot \text{CH}_2 \\ \text{N} = \text{N} \end{matrix} > \text{C} : \text{CH} \cdot \text{CO}_2\text{H}$, pre-

pared by heating the preceding ester with hydrochloric acid, separates from ether in minute, colourless prisms and melts at 184—185°; the *barium* derivative, $\text{C}_4\text{H}_3\text{O}_3\text{N}_3\text{Ba} \cdot \text{H}_2\text{O}$, forms sparingly soluble, colourless needles.

T. M. L.

Triazines. LUDWIG WOLFF and HANS LINDENHAYN (*Ber.*, 1903, **36**, 4126—4129).—Wolff (*Abstr.*, 1903, i, 205) has described the preparation of acetophenoneazocyanide, $\text{COPh} \cdot \text{CH}_2 \cdot \text{N} : \text{N} \cdot \text{CN}$, from hydrogen cyanide and diazoacetophenone. When acetophenoneazocyanide is dissolved in concentrated hydrochloric acid, it forms a substance which melts at 95° and is probably the aminochloride,



on crystallisation from alcohol, hydrogen chloride is eliminated and

3-chloro-5-phenyltriazine, $\text{CPh} \begin{matrix} \text{CH} \cdot \text{N} \\ \text{N} : \text{CCl} \end{matrix} > \text{N}$, is produced; this separates

from alcohol in colourless needles or prisms and melts at 122—123°. It yields 3-hydroxy-5-phenyltriazine (Wolff, *loc. cit.*) when boiled with a dilute aqueous solution of potassium carbonate.

Acetophenoneazothioformamide, $\text{COPh}\cdot\text{CH}_2\cdot\text{N}:\text{N}\cdot\text{CS}\cdot\text{NH}_2$, prepared by passing hydrogen sulphide through an aqueous solution of the potassium salt of acetophenoneazocyanide, separates from alcohol in yellow prisms and melts at 170°. It yields 3-thio-5-phenylhydrotriazine, $\text{CPh}\langle\begin{smallmatrix}\text{CH}-\text{N} \\ \text{NH}\cdot\text{CS}\end{smallmatrix}\rangle\text{N}$, when boiled with potassium carbonate solution and then acidified; this separates from alcohol in red needles, melts at 200°, has the properties of a mercaptan, and readily dissolves in alkali carbonates to form bright yellow salts. When boiled with 20 per cent. nitric acid, it forms the *disulphide*, $(\text{C}_6\text{H}_5\text{N}_3)_2\text{S}_2$, which crystallises from benzene in yellow prisms and melts at 183°. A. McK.

Compounds with Two and Three Azine Rings. OSCAR HINSBERG and E. SCHWANTES (*Ber.*, 1903, 36, 4039—4050).—The compound obtained by Bladin (*Abstr.*, 1885, 784) by the action of cyanogen on *o*-phenylenediamine is probably 1:2-diaminoquinoxaline of the formula $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{N}:\text{C}\cdot\text{NH}_2 \\ \text{N}:\text{C}\cdot\text{NH}_2\end{smallmatrix}\rangle$, and condenses with *o*-quinones, oxalic acid, and α -keto-acids in accordance with this constitution. It reacts with benzil in glacial acetic acid solution, forming *diphenylpyrazinophenazine*, $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{N}:\text{C}\cdot\text{N}:\text{CPh} \\ \text{N}:\text{C}\cdot\text{N}:\text{CPh}\end{smallmatrix}\rangle$, which separates from methyl alcohol in red crystals and melts at 235°, dissolving readily in alcohol, acetone, chloroform, or glacial acetic acid, less readily in ether, insoluble in water. The solution in concentrated sulphuric acid is intensely violet, and deposits a red precipitate on dilution.

Hydroxymethylpyrazinophenazine, $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{N}:\text{C}\cdot\text{N}:\text{CMe} \\ \text{N}:\text{C}\cdot\text{N}:\text{C}\cdot\text{OH}\end{smallmatrix}\rangle$, from pyruvic acid, crystallises from dilute acetic acid in small, bright yellow needles melting at above 300° and dissolving readily in acetic acid, sparingly in water or alcohol. The azine dissolves in potassium hydroxide to a colourless solution, and in mineral acids to slightly yellow solutions.

Dihydroxypyrazinophenazine, from diaminoquinoxaline and oxalic acid at 160°, forms yellowish-white crystals melting at above 300°, almost insoluble in water or organic solvents, but dissolving in dilute acids or alkali hydroxides. The *ammonium* salt, $\text{C}_{10}\text{H}_6\text{O}_2\text{N}_4\cdot\text{NH}_3$ resembles the azine.

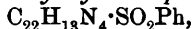
Quinoxalophenanthrazine, $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{N}:\text{C}\cdot\text{N} \\ \text{N}:\text{C}\cdot\text{N}\end{smallmatrix}\rangle\text{C}_{14}\text{H}_8$, from phenanthraquinone, crystallises from glacial acetic acid in red needles and melts at 200°, dissolving readily in chloroform, sparingly in alcohol, ether, benzene, or acetone. The *hydrochloride* is a black, unstable powder, decomposing in air. Alcoholic ammonium sulphide reduces the base to *dihydroquinoxalophenanthrazine*, $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{N}:\text{C}\cdot\text{NH} \\ \text{N}:\text{C}\cdot\text{NH}\end{smallmatrix}\rangle\text{C}_{14}\text{H}_8$, crystal-

lising from glacial acetic acid in small, yellowish-brown needles melting above 300° , and almost insoluble in alcohol, ether, benzene, or chloroform, the traces that dissolve producing a green fluorescence. Potassium dichromate re-oxidises it to the original azine. *Dihydroquinoxalophenanthrazine phenylsulphone*, $C_{22}H_{18}N_4 \cdot SO_2Ph$, from the azine and benzenesulphonic acid, may be obtained in crystalline form by addition of water to the acetic acid solution, and dissolves very sparingly in alcohol, acetone, benzene, or ether to solutions with yellowish-green fluorescence, more readily in acetic acid or chloroform, and melts at above 300° . With phosphorus pentachloride, 2:3-dihydroxynaphthaquinoxaline (Kühling, Abstr., 1891, 1341) yields

2:3-dichloronaphthaquinoxaline, $C_{10}H_6 \begin{smallmatrix} N:CCl \\ | \\ N:CCl \end{smallmatrix}$, separating from alcohol as a slightly yellow powder melting at 142° , insoluble in water, but dissolving readily in acetic acid or chloroform, and not decomposed by 10 per cent. potassium hydroxide at 100° . When heated at 160° with 1:2-naphthylenediamine in a current of carbon dioxide, it

forms *dinaphthafluoflavine*, $C_{10}H_6 \begin{smallmatrix} N:C \cdot NH \\ | \\ N:C \cdot NH \end{smallmatrix} C_{10}H_6$, which crystallises from glacial acetic acid in small, brownish-yellow needles, darkening without melting at about 300° , dissolving very sparingly in alcohol, benzene, or chloroform to slightly fluorescent solutions. Potassium dichromate oxidises it to *naphthaquinoxalonaphthazine*,

$C_{10}H_6 \begin{smallmatrix} N:C \cdot N \\ | \\ N:C \cdot N \end{smallmatrix} C_{10}H_6$, crystallising from chloroform in intensely red needles and decomposing at about 300° . Stannous chloride or ammoniacal ammonium sulphide reduce it to the flavine. Benzenesulphonic acid forms *dinaphthafluoflavine phenylsulphone*,



crystallising from its green fluorescent solution in acetic acid in yellowish-red needles melting above 300° . Potassium dichromate oxidises it to an intensely red compound, probably a sulphonazine.

2:3-Dichloronaphthaquinoxaline reacts with *o*-phenylenediamine, forming *naphthafluoflavine*, $C_6H_4 \begin{smallmatrix} N:CH \cdot NH \\ | \\ N:CH \cdot NH \end{smallmatrix} C_{10}H_6$ (compare Abstr., 1902, i, 238).

Fluorubine, $C_6H_4 \begin{smallmatrix} N:C \cdot NH \cdot C:N \\ | \\ N:C \cdot NH \cdot C:N \end{smallmatrix} C_6H_4$, prepared by heating dichloroquinoxaline with diaminoquinoxaline and decomposition of the hydrochloride formed, is a yellow, crystalline powder, very sparingly soluble in organic solvents, and dissolving both in acids and alkalis to solutions with red fluorescence. Sodium ethoxide precipitates the brown *sodium salt*. The *hydrochloride*, $2C_{16}H_{10}N_6 \cdot 3HCl$, forms glistening, golden leaflets decomposed by water.

3-Chloro-2-aminonaphthaquinoxaline, $C_{10}H_6 \begin{smallmatrix} N:C \cdot NH_2 \\ | \\ N:CCl \end{smallmatrix}$, prepared by heating dichloronaphthaquinoxaline with alcoholic ammonia under pressure, crystallises from glacial acetic acid in long, colourless needles

melting and darkening at 222°. The yellow *hydrochloride* is insoluble in excess of acid.

Dichloroquinoxaline and dry ethylamine at 120° form *diethylhydrazinoquinoxaline*, $C_6H_4 \begin{smallmatrix} \diagup N:CH \cdot NHEt \\ \diagdown N:CH \cdot NHEt \end{smallmatrix}$, crystallising from dilute alcohol in colourless needles and melting at 156°, dissolving readily in most organic solvents, insoluble in water. C. H. D.

Strain-laws of Ring-systems. OSCAR HINSBERG (*Ber.*, 1903, 36, 4051—4054).—Further experiments have been made to test the conclusions as to the stability of azine-rings arrived at by the author (*Abstr.*, 1902, i, 238). Azines containing 5 rings in linear order have not been prepared, and fluorubine, which is a dihydro-compound of such an azine (see preceding abstract), is not oxidisable to the azine, and the latter is therefore unstable, even if capable of existence. The properties of β -naphthacridine and γ -naphthacridine (Strohbach, *Abstr.*, 1902, i, 183), are also shown to confirm the same laws. C. H. D.

A Condensation Product of Indoxylic Acid and Nitrosoantipyrine. HEINRICH BECHHOLD (*Ber.*, 1903, 36, 4131—4135).—When molecular quantities of nitrosoantipyrine and indoxylic acid in alcoholic solution are boiled, the compound, $\begin{smallmatrix} NMe \cdot CMe \\ | \\ NPh - CO \end{smallmatrix} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} C:N:C \begin{smallmatrix} \diagdown CO \\ \diagup NH \end{smallmatrix} C_6H_4$, separates as brown, glistening crystals which melt and decompose at 269° (corr.). Its *picrate* melts and decomposes at 174—176°. Dilute sulphuric acid converts the compound into isatin and aminoantipyrine. A. McK.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. III. Dihydrotetrazines. ROBERT STOLLÉ (*J. pr. Chem.*, 1903, [ii], 68, 464—468. Compare *Abstr.*, 1903, i, 721; this vol., i, 102).—When heated at 180°, butyrylhydrazide yields 80 per cent. of the theoretical amount of 3:6-dipropyl-1:4-dihydro-1:2:4:5-tetrazine (compare Pellizzari, *Abstr.*, 1897, i, 231; 1899, i, 858; Hantzsch and Silberrad, *Abstr.*, 1900, i, 261). When heated at 200—250°, benzoylhydrazide yields 3:6-diphenyl-1:4-dihydro-1:2:4:5-tetrazine, dibenzoylhydrazide, 3:5-diphenyloxadiazole, and 2:5-diphenyl-1:3:4-triazole. The diphenyltriazole is probably formed by the action of heat on diphenyldihydrotetrazine, as diundecyldihydrotetrazine yields diundecyltriazole on distillation. 1:4-Dihydro-1:2:4:5-tetrazine is formed by the action of ethyl orthoformate on hydrazine hydrate at 120°. When shaken with benzaldehyde, it yields a condensation product which melts at 170°. G. Y.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. IV. Osotetrazines. ROBERT STOLLÉ (*J. pr. Chem.*, 1903, [ii], 68, 469—471. See foregoing abstract).—The action of iodine on the silver derivative of glyoxaldibenzosazone leads to the formation of *s*-diphenyldioxadiazole and of glyoxaldibenzosazone. With the mercuric chloride derivative of benzildibenzosazone, the action of iodine leads to the formation of 2:3-dibenzoyl-5:6-diphenyl-2:3-di-

hydro-1:2:3:4-tetrazine. When boiled with aqueous alcoholic hydrochloric acid, the dibenzoyl derivative is partly hydrolysed with formation of *benzoyldiphenyldihydrotetrazine*, which is further hydrolysed to diphenyldihydrotetrazine by prolonged boiling with concentrated acids. The iminohydrogen atom of the monobenzoyl derivative is replaceable by metals.

5:6-*Diphenyl-2:3-dihydro-1:2:3:4-tetrazine* yields a *silver* derivative with sodium ethoxide and silver nitrate; with hydrogen chloride in ethereal solution, it forms a *hydrochloride* which is hydrolysed by water. By the action of bromine water, it is converted into nitrogen and tolane dibromide, by the action of nitrous acid or amyl nitrite into diphenylosotriazole. With benzaldehyde, diphenyldihydrotetrazine yields a stable condensation product, $\begin{matrix} \text{CPh}\cdot\text{N}\cdot\text{N} \\ | \\ \text{CPh}\cdot\text{N}\cdot\text{N} \end{matrix} > \text{CHPh}$. From attempts to decompose diphenyldihydrotetrazine by heating with acids, only small quantities of hydrazine have been obtained. G. Y.

Azoxy-compounds. ALFRED WOHL [and O. AHLERT] (*Ber.*, 1903, 36, 4139—4143. Compare *Abstr.*, 1901, i, 612).—Phenazine-5:10-oxide is not transformed into hydroxyphenazine when heated with sulphuric acid. At 200°, no change occurs, and at 240—250° phenazine is formed.

Azoxybenzene yields an unstable *dibromide*, $\text{C}_{12}\text{H}_{10}\text{ON}_2\text{Br}_2$, which on exposure to the air rapidly gives up bromine. Phenazine 5:10-oxide also yields a brown crystalline *dibromide*, $\text{C}_{12}\text{H}_8\text{ON}_2\text{Br}_2$, melting at 132—133° and readily decomposed by alkalis. A *hydrobromide*, $\text{C}_{12}\text{H}_8\text{ON}_2\text{Br}_2\cdot\text{HBr}$, melting at 212—215°, has also been obtained. The *hydrochloride* of phenazine 5:10-oxide, $\text{C}_{12}\text{H}_8\text{ON}_2\text{HCl}$, crystallises in orange-red needles, and when heated, loses hydrogen chloride and gives the free oxide.

On nitration with sulphuric and nitric acids, the oxide yields a mixture of two *dinitro*-derivatives. The one melts at 269° and is almost insoluble in acetone, the other melts at 240°, and is somewhat more readily soluble in acetone. J. J. S.

Diazo-compounds. ARTHUR HANTZSCH (*Ber.*, 1903, 36, 4361—4366).—Controversial, in reply to Euler (this vol., i, 119). C. H. D.

Isomerism of Diazoxides. EUGEN BAMBERGER (*Ber.*, 1903, 36, 4054—4055).—The author's view that normal diazoxides are to be regarded as metallic diazonium salts, $\begin{matrix} \text{Ar}\cdot\text{N}:\text{N} \\ | \\ \text{OM} \end{matrix}$, and the *isodiazoxides* as metal-substituted diazohydroxides, $\text{Ar}\cdot\text{N}:\text{N}\cdot\text{OM}$, was abandoned on account of the difficulty of regarding a base such as diazonium hydroxide as an acid. This difficulty is now removed by the work of von Zawidecki (*Abstr.*, 1903, i, 801), which shows that the absence of hydrolysis of alkali salts of non-conducting acids occurs not only in the case of pseudo-acids, but also with many amphoteric electrolytes. Diazonium hydroxide is thus to be regarded as an amphoteric electrolyte, capable of forming salts with bases as well as with acids. C. H. D.

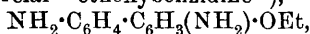
Toluene-*p*-diazonium Sulphate and the Action of Sulphuric Acid on *p*-Tolyl Methyl Ether. GELLERT ALLEMAN (*Amer. Chem. J.*, 1904, 31, 24—45. Compare Chamberlain, *Abstr.*, 1897, i, 562; Metcalf, *Abstr.*, 1893, i, 585).—Diazo-*p*-toluene sulphate crystallises in lustrous, white flakes or transparent prisms, and is comparatively stable.

When *p*-methoxytoluene, obtained by the action of methyl alcohol on the diazonium compound, is heated with concentrated sulphuric acid, *p*-methoxytoluene-*m*-sulphonic acid is produced, which crystallises from alcohol in long, colourless, hexagonal prisms, melts at 105—108°, and is very soluble in water; its barium, sodium, potassium, calcium, magnesium, copper, zinc, and lead salts are described. When this acid is fused with potassium hydroxide at a comparatively low temperature, potassium *p*-hydroxytoluene-*m*-sulphonate is formed, whilst at higher temperatures methylcatechol seems to be produced.

By the oxidation of *p*-methoxytoluene-*m*-sulphonamide with potassium permanganate, *p*-methoxy-*m*-sulphaminebenzoic acid is obtained, which crystallises in needles or plates, melts at 276—277°, and is soluble in hot alcohol; its sodium, potassium, calcium, magnesium, and barium salts are described. If *p*-methoxy-*m*-sulphaminebenzoic acid is cautiously fused with potassium hydroxide, *p*-hydroxy-*m*-sulphaminebenzoic acid is formed, whilst on prolonged fusion at a high temperature, protocatechuic acid is produced. *p*-Hydroxy-*m*-sulphaminebenzoic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{SO}_2\cdot\text{NH}_2$, forms radiating clusters of crystals, melts at 258°, decomposes at about 265°, and is soluble in water or alcohol; its sodium and barium salts are described. E. G.

Acid Reduction of *o*-Ethoxy- and *m*-Methoxy-azobenzenes. PAUL JACOBSON, GEORG FRANZ, and FRITZ HÖNIGSBERGER (*Ber.*, 1903, 36, 4069—4082).—With the view of determining whether the semidine transformation of hydrazo-compounds takes place more readily in cases where the substituent in the hydrazo-compound is in a position other than the para-, the authors have studied the reduction in acid solution of *o*-ethoxy- and *m*-methoxy-azobenzenes. It is shown that the corresponding benzidine bases are formed in good yields in both cases, whilst the semidine bases are formed either not at all or in very small amounts.

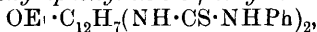
o-Ethoxyazobenzene, $\text{N}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$, prepared by condensation of nitrosobenzene with *o*-phenetidine, separates from light petroleum in red, monoclinic plates and melts at 43—44°. When reduced by zinc dust in boiling alcoholic alkaline solution, it forms *o*-ethoxyhydrazobenzene, $\text{NHPh}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$, which crystallises from light petroleum in white needles and melts at 66°. When *o*-ethoxyazobenzene is reduced by stannous chloride and hydrochloric acid, 3-ethoxy-4:4'-diaminodiphenyl (the commercial "ethoxybenzidine"),



melting at 139° is obtained. Its solution in hydrochloric acid gives an intense orange-red coloration with ferric chloride, which disappears on the addition of concentrated acid. Its *bis-o*-hydroxybenzylidene derivative, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_3(\text{OEt})\cdot\text{N}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, prepared by allowing an alcoholic solution of *o*-ethoxybenzidine and salicylaldehyde to re-

main at the ordinary temperature for 24 hours, crystallises from benzene in yellow needles and melts at 136—137°. The *bis-p-methoxybenzylidene* derivative, prepared from *o*-ethoxybenzidine and anisaldehyde, separates from a mixture of benzene and light petroleum in microscopic needles and melts at 146—147°. The *bis-p-nitrobenzylidene* derivative, $\text{OEt}\cdot\text{C}_{12}\text{H}_7(\text{N}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$, crystallises from benzene in dark red needles and melts indefinitely at 182—183°. The *bis-cinnamylidene* derivative, $\text{OEt}\cdot\text{C}_{12}\text{H}_7(\text{N}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHPh})_2$, prepared from *o*-ethoxybenzidine and cinnamaldehyde, separates from a mixture of benzene and light petroleum in tiny yellow needles and melts at 167—168°.

When an alcoholic solution of ethoxybenzidine is warmed with phenylcarbimide, *ethoxydiphenylene-bis-phenylthiocarbamide*,

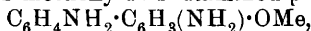


is produced; when this is heated with 30 per cent. sulphuric acid at 150°, ethoxybenzidine sulphate is formed.

That the ethoxy-group in the ethoxybenzidine examined is in the *o*-position relatively to the amino-group was proved by diazotising the compound and boiling the product with alcohol, when 3-ethoxydiphenyl was formed (compare following abstract); this melts at 34° and boils at 305° under atmospheric pressure.

By the transformation of *o*-ethoxyhydrazobenzene, only one base, namely, *o*-ethoxybenzidine, is formed.

m-Methoxyazobenzene (compare following abstracts) was reduced in acid solution by stannous chloride and yielded, as the main product, *m*-methoxybenzidine (2-methoxy-4 : 4'-diaminodiphenyl),



which crystallises from a mixture of benzene and light petroleum in stellate plates and melts at 103—103·3°. The *picrate* of *m*-methoxybenzidine begins to decompose at 200° and melts and decomposes at 220°. Its *bis-p-methoxybenzylidene* derivative crystallises from benzene in yellow needles and melts at 150°. Its *diacetyl* derivative, $\text{OMe}\cdot\text{C}_{12}\text{H}_7(\text{NH}\cdot\text{COMe})_2$, melts and decomposes at 285°.

By the diazotisation of *m*-methoxybenzidine and subsequent action of alcohol, the diazo-groups were apparently replaced not by hydrogen, but by the ethoxy-groups. The elimination of the amino-groups from *m*-methoxybenzidine was successfully accomplished, however, by reducing the diazo-derivative to the corresponding dihydrazine and then oxidising the latter by means of copper sulphate to 2-methoxydiphenyl, melting at 29°.

m-Methoxyhydrazobenzene undergoes benzidine transformation to *m*-methoxybenzidine to the extent of at least from 75—80 per cent. With regard to its semidine transformation, there was no evidence for the formation of a *p*-semidine, but an *o*-semidine was apparently formed to the extent of not more than about 5 per cent. A. McK.

***m*-Compounds of Diphenyl. Constitution of the Diphenyl Bases Derived from *p*-Substituted Hydrazo-compounds.** PAUL JACOBSON and ARTHUR LOEB (*Ber.*, 1903, 36, 4082—4093. Compare preceding abstract).—In order to establish the constitution of the ethoxydiphenyl obtained from 4 : 4'-diamino-3-ethoxydiphenyl, *m*-hydr.

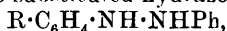
oxydiphenyl and its ethyl ether have been synthesised by the authors from *m*-nitroaniline.

m-Nitroaniline was diazotised and the potassium *m*-nitroisodiazobenzene, obtained by the action of the diazonium solution on a strong solution of potassium hydroxide, was converted into *m*-nitrodiphenyl by means of acetyl chloride and benzene, thus: $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{N} \cdot \text{OK} + \text{C}_6\text{H}_6 + \text{CH}_3 \cdot \text{COCl} = \text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{Ph} + \text{N}_2 + \text{KCl} + \text{CH}_3 \cdot \text{CO}_2\text{H}$. 3-Nitrodiphenyl separates from aqueous alcohol in bright yellow, tetragonal leaflets and melts at 61° . Its constitution was further determined by oxidising it with chromic acid, when *m*-nitrobenzoic acid was produced.

3-Aminodiphenyl, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{Ph}$, prepared by the reduction of 3-nitrodiphenyl with tin and hydrochloric acid, boils at $176-178^\circ$ under 18 mm. pressure, and solidifies to stellate groups of needles which melt at 30° . When the diazonium salt is decomposed with water, it forms 3-hydroxydiphenyl, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{Ph}$, which crystallises in glistening, white needles melting at 78° .

3-Ethoxydiphenyl, prepared by boiling an alcoholic solution of 3-hydroxydiphenyl with sodium ethoxide and ethyl iodide, distils at $160-161^\circ$ under 9 mm. pressure yielding a colourless oil, which quickly crystallises and then melts at $34-35^\circ$. It is identical with the ethoxydiphenyl obtained from 4:4-diamino-3-ethoxydiphenyl (compare preceding abstract), and yields *m*-hydroxydiphenyl when heated with hydriodic acid.

Certain *p*-substituted hydrazo-compounds undergo rearrangement in such a manner that the main product is not that of the benzidine transformation, but the amino-compounds produced are primary diamines of the diphenyl series. Those diphenyl bases, $\text{C}_{12}\text{H}_7\text{R}(\text{NH}_2)_2$, which are formed from *p*-substituted hydrazo-compounds,

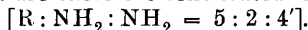


contain the substituent R in the meta-position relatively to that where the benzene rings join. This view was confirmed by transforming *p*-acetoxyhydrazobenzene into diaminohydroxydiphenyl, removing the amino-groups from the latter, and then converting the product into its ethyl ether, which was found to be identical with 3-ethoxydiphenyl.

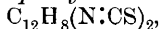
Diphenyl bases, formed from *p*-substituted hydrazo-compounds, contain one amino-group, heteronuclear to the substituent R and in the para-position relatively to that where the benzene rings join. This was confirmed by the oxidation of hydroxybisacetylaminodiphenyl to *p*-acetylaminobenzoic acid.

The diphenyl bases in question accordingly contain the amino-groups in the positions 2:4' (diphenylene position). This was proved in the case of chlorodiaminodiphenyl, from which the chlorine was removed by dissolving the base in hot alcohol and then adding an excess of sodium; the resulting product was identified as isobenzidine by its conversion into its bis-*o*-hydroxybenzylidene derivative by aid of salicylaldehyde.

The diphenyl bases are therefore constituted thus:



isoBenzidine may be further characterised by its conversion into diphenylenedithiocarbimide (diphenyl-2:4'-dithiocarbimide),



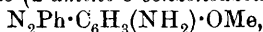
produced by the action of a chloroform solution of thiophosgene on an aqueous solution of isobenzidine containing a little hydrochloric acid; this substance separates from light petroleum in needles and melts at 94° . By the action of ammonia, it is converted into *diphenylenebis-thiocarbamide* (2:4'-bisthioureidodiphenyl), $C_{12}H_8(NH \cdot CS \cdot NH_2)_2$, which forms glassy plates melting at 201° .

Diphenylenebisphenylthiocarbamide, $C_{12}H_8(NH \cdot CS \cdot NHPh)_2$, formed from aniline and diphenylenedithiocarbimide, melts at 164° .

A. McK.

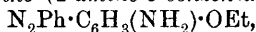
***m*-Hydroxyazobenzene.** Constitution of *p*-Hydroxyazo-compounds. PAUL JACOBSON and FRITZ HÖNIGSBERGER (*Ber.*, 1903, 36, 4093—4123).—Although compounds containing the hydroxyl group in the meta-position relatively to the azo-group are known, the simplest type of such *m*-hydroxyazo-compounds, namely, *m*-hydroxyazobenzene, $OH \cdot C_6H_4 \cdot N_2 \cdot Ph$, had not previously been isolated. The authors have prepared and studied this compound with the particular aim of throwing light on the debated question as to the constitution of *o*- and *p*-hydroxyazo-compounds.

Benzeneazo-o-anisidine (2-amino-5-benzeneazoanisole),



prepared by combining *o*-anisidine with diazobenzene, separates from toluene in reddish-brown plates and melts at 110.5 — 111.5° .

Benzeneazo-o-phenetidine (2-amino-5-benzeneazophenetole),



prepared in an analogous manner from *o*-phenetidine, crystallises from light petroleum in orange-yellow needles and melts at 109 — 110.5° . When acted on by stannous chloride, it undergoes decomposition into aniline and 2:5-diaminophenetole, which were identified by the formation from them of benzanilide and 2:5-bisbenzaminophenetole (m. p. 213°) (compare succeeding abstract).

Benzeneazo-m-anisole (3-methoxyazobenzene), $N_2Ph \cdot C_6H_4 \cdot OMe$, prepared from benzeneazo-*o*-anisidine by diazotisation and reduction of the diazonium compound by alcohol, boils at 193 — 193.5° (corr.) under 15 mm. pressure and melts at 32.7 — 32.8° .

Benzeneazo-m-phenetole (3-ethoxyazobenzene), $N_2Ph \cdot C_6H_4 \cdot OEt$, prepared in an analogous manner by removal of the amino-groups from benzeneazo-*o*-phenetidine, separates from light petroleum in tetragonal plates, melts at 63.5 — 64° , and boils at about 200° under 22 mm. pressure. Its constitution was further proved by reducing it to the corresponding hydrazo-compound, which, when heated with alcoholic potash and zinc dust at 160° , yields aniline and *m*-phenetidine. The latter was identified by its melting point and by its conversion into *phenyl-m-phenetylthiocarbamide*, $NHPh \cdot CS \cdot NH \cdot C_6H_4 \cdot OEt$, melting at 138.5° .

m-Hydroxyazobenzene, $N_2Ph \cdot C_6H_4 \cdot OH$, prepared by hydrolysing benzeneazo-*m*-anisole or benzeneazo-*m*-phenetole by aluminium chloride, crystallises from benzene in amber-coloured prismatic rods; it softens at 112° and melts mainly at 112 — 114° when quickly heated. Its solution in dilute alkalis and in concentrated hydrochloric acid is of

a deep orange-red colour. Its *sodium* salt forms yellow needles; its *acetyl* derivative separates from light petroleum in orange-coloured, glassy plates and melts at 67.5° ; its *benzoyl* derivative separates from light petroleum in glistening red plates and melts at $91.5-92^{\circ}$.

m-Hydroxyazobenzene is contrasted with its ortho- and para-isomerides. *m*- and *p*-Hydroxyazobenzene form salts with bases much more readily than does *o*-hydroxyazobenzene. The hydrochlorides of *m*- and *p*-hydroxyazobenzenes are stable, but the hydrochloride of *o*-hydroxyazobenzene is unstable at the ordinary temperature. The hydrochlorides also differ in solubility; the platinichlorides are also contrasted. The cryoscopic behaviour of the meta-compound in naphthalene solution has been studied; its behaviour resembles that of the para-compound, and is different from that of the meta-compound.

m-Hydroxyazobenzene is readily reduced to the corresponding hydrazo-compound, in this respect differing from *o*- and *p*-hydroxyazobenzenes, which yield aniline and the corresponding aminophenols on reduction. *m*-Hydroxyhydrazobenzene, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NHPh}$, prepared by reducing *m*-hydroxyazobenzene by zinc dust and glacial acetic acid, separates from a mixture of benzene and light petroleum in glistening, colourless needles and melts at $126-126.5^{\circ}$. It is an unusual type of hydrazo-compound, since it contains a hydroxyl group, to the presence of which its solubility in water is doubtless due.

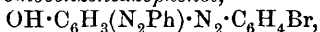
m-Ethoxyhydrazobenzene, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NHPh}$, prepared by reduction of *m*-ethoxyazobenzene, crystallises from light petroleum in silky needles and melts at $74-75^{\circ}$.

m-Hydroxybenzidine (4:4'-diamino-2-hydroxydiphenyl), prepared by reducing *m*-hydroxyazobenzene in acid solution, crystallises from water in leaflets and melts at $226-227^{\circ}$; it is also readily prepared by the rearrangement of *m*-hydroxyhydrazobenzene; it may also be obtained from *m*-methoxybenzidine by hydrolysing it with hydriodic acid and red phosphorus. Its *bis-p-methoxybenzylidene* derivative,

$\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, prepared from *m*-hydroxybenzidine and anisaldehyde, crystallises from xylene in yellow needles and melts at 200° .

Bisazo-compounds were also prepared from *m*-hydroxyazobenzene, the entrant group, $\cdot\text{N}_2\text{R}$, taking up a para-position relatively to the hydroxyl group in the original hydroxyazobenzene.

3-Benzeneazo-4-*p*-bromobenzeneazophenol,

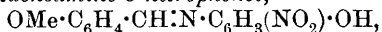


prepared by diazotising *p*-bromoaniline to form a solution of *p*-bromodiazobenzene and then acting on the latter with an alkaline solution of *m*-hydroxyazobenzene, forms yellow needles and decomposes at about 115° . Its *benzoyl* derivative forms stellate groups of red crystals and melts at $175-176.5^{\circ}$. The constitution of 3-benzeneazo-4-*p*-bromobenzeneazophenol was determined by reducing it to 3:4-diaminophenol (compare following abstract).

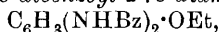
The bearing of the authors' results on the constitution of hydroxyazo-compounds is discussed and the conclusion drawn that *p*-hydroxyazo-compounds, not only in the form of their metallic salts, alkyl ethers, and acyl derivatives, but also in the free state, are true azo-compounds and are not quinone-hydrazones. This conclusion presupposes the non-

existence of *m*-quinones; it is in opposition to the views advanced by Hantzsch and others. A. McK.

Diaminophenols. PAUL JACOBSON and FRITZ HÖNIGSBERGER (*Ber.*, 1903, 36, 4124—4126. Compare preceding abstract).—*2-p-Methoxybenzylideneamino-5-nitrophenol*,



prepared by heating molecular amounts of anisaldehyde with 2-amino-5-nitrophenol at 160°, crystallises from benzene in prismatic plates and melts at 160—161°. When sodium ethoxide is slowly added to its alcoholic solution mixed with ethyl bromide, anisaldehyde is eliminated and ethylation takes place with formation of 5-nitro-2-aminophenetole, $\text{NH}_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{OEt}$, which crystallises in yellow needles melting at 91°. On reduction, it yields 2:5-diaminophenetole, which was converted into *dibenzoyl-2:5-diaminophenetole*,



by benzoylation. This separates from aqueous alcohol in asbestos-like needles and melts at 213°.

Dibenzoyl-3:4-diaminophenol benzoate, $\text{C}_6\text{H}_3(\text{NHBz})_2 \cdot \text{OBz}$, prepared by benzoylating the reduction product of 3-nitro-4-aminophenol, separates from alcohol in needles and melts at 225°. When hydrolysed, it forms dibenzoyldiaminophenol, which crystallises in glistening plates, which melt at 203—205°. A. McK.

[*β*-Naphtholazo-*α*-naphthol-5-sulphonic Acid.] FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 145906).—The diazonium compounds of 1-chloro-*β*-naphthylamine-5-sulphonic acid and of *β*-naphthylamine-1:5-disulphonic acid are decomposed by prolonged warming with sodium carbonate, the chlorine atom in the first case and the 1-sulphonic group in the second case being replaced by hydroxyl, forming 2-diazo-*α*-naphthol-5-sulphonic acid, which combines with *β*-naphthol to form a brownish-violet dye. C. H. D.

[Azo-compounds from Acyl-*p*-aminophenols.] DAHL & Co. (D.R.-P. 146265).—*p*-Aminophenol does not combine with diazonium salts, but combination is readily produced when the formyl or acetyl derivative is employed in alkaline solution. Azo-compounds were obtained with diazotised naphthionic acid, 4-aminoaceto-*α*-naphthalide-6-(or 7-)-sulphonic acid, and *β*-naphthylamine-8-sulphonic acid. *Formyl-p-aminophenol* crystallises from water in groups of small needles and melts at 139—140°. C. H. D.

Azo- and Azomethine Derivatives of 2-Aminoanthraquinone. FELIX KAUFLEDER (*Zeit. Farb. Text.-Chem.*, 1903, 2, 469—473).—2-Aminoanthraquinone is diazotised by converting it into its hydrochloride in glacial acetic acid solution and subsequently adding a 30 per cent. excess of amyl nitrite; it is easily soluble in acetic acid, is precipitated by ether, and is stable at the ordinary temperature. The following compounds were prepared by coupling it with phenols. *Anthraquinone-2-azophenol*, $\text{C}_{20}\text{H}_{12}\text{O}_3\text{N}_2$, crystallises from anisole and decomposes at 290°. *Anthraquinone-2-azo-*α*-naphthol* separates from the same solvent as a red, crystalline mass and melts at about 278°. *Anthraquinone-2-azo-*β*-naphthol* forms long, scarlet needles and melts at

262—264°. *Anthraquinone-2-azo-β-naphthol-7-sulphonic acid* is moderately soluble in hot water. *Anthraquinone-2-azoresorcinol* separates from glacial acetic acid as a red, crystalline mass and melts and decomposes at 261—263°. *Anthraquinone-2-azosalicylic acid* crystallises from alcohol in a flocculent mass and melts and decomposes at 270°. *Anthraquinone-2-azomethylaniline* and *anthraquinone-2-azodimethylaniline* crystallise from amyl alcohol in needles and melt at 264—266° and 202—204° respectively.

The following compounds were obtained by condensing 2-aminoanthraquinone with aldehydes. *Benzylidene-2-aminoanthraquinone*, $C_6H_4:(CO)_2:C_6H_3:N:CHPh$, separates from toluene or anisole in light yellow or brown crystals and melts at 185—187°. *o-Hydroxybenzylidene-2-aminoanthraquinone* forms golden-yellow needles and melts at 229—231°; the analogous *p-derivative* crystallises from nitrobenzene in dark golden-yellow needles melting at 258°. *o-, m-, and p-Nitrobenzylidene-2-aminoanthraquinones* melt respectively at 216—218°, 245—246°, and 246—249°, and vary in colour from yellow to brownish-yellow.

The colour relationship of the foregoing substances is discussed.

W. A. D.

Azo-compound from 3:6-Diaminoquinol Dialkyl Ethers and 1:8-Dihydroxynaphthalene 3:6-disulphonic Acid ["Chromotrope"] Acid. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 146210).—The dialkyl ethers of 3:6-diaminoquinol (Nietzki and Rechberg, Abstr., 1890, 967) may be diazotised and then combined with "chromotrope" acid, forming a blue azo-compound, $NH_2 \cdot C_6H_2(OAlk)_2 \cdot N:N \cdot C_{10}H_3(OH)_2(SO_3H)_2$. The same product is obtained on diazotising the acetyl derivative, combining with "chromotrope" acid, and hydrolysing, or by diazotising the nitroamino-ether, combining with the acid, and reducing the nitro-group with sodium sulphide.

C. H. D.

Isomerism of the Salts of Aminoazobenzene. JOHANNES THIELE (*Ber.*, 1903, 36, 3965—3967).—A red hydrochloride of aminoazobenzene can be prepared by adding ethereal hydrogen chloride to an ethereal solution of the base; the salt is stable when dry and free from acid, but is converted into the ordinary violet salt by acids, by heating, and by pressure. The red salt also separates when an aqueous solution of the hydrochloride is precipitated by means of sodium chloride.

T. M. L.

Action of Carbon Dioxide on Aqueous Solutions of Aniline in the presence of Nitrites. LOUIS MEUNIER (*Compt. rend.*, 1903, 137, 1264—1266).—Aniline reacts with sodium nitrite in aqueous solution, saturated with carbon dioxide, to form diazoaminobenzene; the reaction proceeds slowly; with silver nitrite under the same conditions, the reaction is much more rapid, and the aniline is converted quantitatively into the silver derivative of diazoaminobenzene, $Ph \cdot N_2 \cdot NPhAg$.

The reaction is explained as follows: the carbon dioxide reacts with the aniline to form aniline carbonate, which undergoes double decom-

position with sodium nitrite to form aniline nitrite, $\text{NH}_2\text{Ph}\cdot\text{NO}_2$; this compound, by the loss of a molecule of water, is transformed into phenylnitrosoamine, $\text{NHPH}\cdot\text{NO}$, which in its tautomeric isodiazio-form $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{OH}$, condenses with aniline to give diazoaminobenzene, $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{NHPH}$. The author finds that the formation of diazoaminobenzene by the action of sodium nitrite in a dilute aqueous solution of aniline (compare Niementowski and Rozskowski, Abstr., 1897, i, 340) is to be attributed to the presence of carbon dioxide dissolved in the water, as pure, boiled, distilled water kept from contact of air gives no precipitate with aniline and sodium nitrite even after a month.

M. A. W.

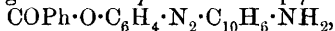
Diazoaminophenols and Hydroxylaminophenols. ALFRED WOHL [and F. GOLDENBERG] (*Ber.*, 1903, 36, 4143—4152).—Free diazoaminophenols may be obtained by hydrolysing their benzoyl esters with cold methyl-alcoholic potassium hydroxide solution in the presence of hydroxylamine.

p-Benzenediazoamino-*p*-phenyl benzoate, $\text{COPh}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{NHPH}$, obtained by the action of aniline on the chloride of *p*-diazophenyl benzoate, crystallises from methyl alcohol in pale yellow plates melting at $132\cdot5^\circ$ (corr.) and is readily soluble in most organic solvents. On hydrolysis, it yields *p*-hydroxydiazoaminobenzene, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{NHPH}$, which may be isolated by passing carbon dioxide into the ice cold aqueous solution. It forms yellow crystals, melts at about 80° , is readily soluble in all the ordinary solvents, including water and light petroleum, and is remarkably unstable. With alcoholic hydrogen chloride, it yields aniline and *p*-hydroxybenzenediazonium chloride.

The *p*-tolyl compound, $\text{COPh}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, forms reddish-yellow crystals, melts at $148\cdot5^\circ$ (corr.) and on hydrolysis yields *p*-hydroxybenzenediazo-*p*-aminotoluene, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, which decomposes at 63° (corr.).

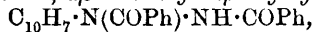
The isomeric *p*-diazo-*o*-toluidinophenyl benzoate melts at 131 — 132° (corr.), but the free hydroxy-derivative is so unstable that it has not been obtained in a pure state.

p-Aminophenol, *m*- and *p*-nitroanilines, and 2:4-dinitroaniline do not react with *p*-diazophenyl benzoate in acetic acid solution. α -Naphthylamine reacts yielding 4-aminonaphthaleneazo-*p*-phenylbenzoate,



which crystallises from benzene in orange-coloured needles melting at 183 — 184° and is insoluble in water or light petroleum. On hydrolysis, it yields 4-hydroxybenzeneazo-4-aminonaphthalene in the form of a red, crystalline powder which sinters at 193° (corr.) and decomposes at 200° (corr.). On reduction and benzylation, it yields the dibenzoyl derivative, $\text{C}_{10}\text{H}_6(\text{NH}\cdot\text{COPh})_2$ [1 : 4], melting at $280\cdot5^\circ$ (corr.), and identical with the compound obtained by benzylation of 1 : 4-naphthylenediamine.

The isomeric compound, $\alpha\beta$ -dibenzoylnaphthylhydrazine,



obtained by benzylation of naphthylhydrazine, melts at 195 — 196° (corr.).

p-Nitrophenyl acetate, when reduced with zinc dust and water in the presence of ammonium chloride and benzene, yields *p*-azoxyphenyl-

acetate, $O < \begin{smallmatrix} N \cdot C_6H_4 \cdot OAc \\ N \cdot C_6H_4 \cdot OAc \end{smallmatrix}$, in the form of pale orange-coloured, felted needles melting at 169° (corr.) When *p*-nitrophenyl benzoate is reduced in hot alcoholic solution with zinc dust and calcium chloride and then shaken with benzaldehyde, *benzylidene-p-hydroxylaminophenyl benzoate*, $O < \begin{smallmatrix} CHPh \\ N \cdot C_6H_4 \cdot O \cdot COPh \end{smallmatrix}$, melting at 205° , is obtained.

Benzylidene-p-aminophenyl benzoate, $COPh \cdot O \cdot C_6H_4 \cdot N : CHPh$, melts at 148° (corr.). J. J. S.

Composition of Gelatin Rendered Insoluble by Chromium Salts and the Theory of the Action of Light on Gelatin in Presence of Chromates. Part I. AUGUSTE LUMIÈRE LOUIS LUMIÈRE and ALPHONSE SEYEWITZ (*Bull. Soc. chim.*, 1903, [iii], 29, 1077—1088. Compare Abstr., 1903, ii, 150).—The precipitation of solutions of gelatin is brought about by many chromic salts and the insolubility of the product in boiling water is most marked in the case of the least acid salts, such as the basic chromic sulphate, $Cr_2(SO_4)_2$ (Recoura, Abstr., 1891, 1430). Precipitation of the gelatin is independent of the nature of the acid radicle of the salt used. No precipitation occurs when solutions of chromium sesquioxide in alkalis are added to solutions of gelatin, but if chromium hydroxide is precipitated in solutions of gelatin, the insoluble gelatin compound is formed unless alkali is added in excess. It was found that 2 grams of chrome alum is the minimum quantity which can be added to 100 grams of gelatin to give a precipitate resistant to boiling water, whilst the maximum amount of the salt which can be absorbed by 100 grams of gelatin is about 21 grams. Chrome alum appears to be absorbed as such by gelatin, but sulphuric acid can be slowly washed out of the insoluble product so formed by boiling water, whence it is probable that the combination occurs between chromium sesquioxide and gelatin. This view is supported by the fact that the ash left on incineration of the precipitate, however prepared, consists only of the oxide.

The gelatin compound, when freshly precipitated, is an elastic, transparent mass having the colour of the salt used in producing it; when washed, it becomes translucent and finally opaque (this form can be obtained at once by the addition of excess of chrome alum to a solution of gelatin in dilute ammonia). When dried, it becomes green in colour and brittle. In this state it contains 3.3 to 3.5 grams of chromium sesquioxide for every 100 grams of gelatin. Both acids and alkalis decompose it, reproducing soluble gelatin.

T. A. H.

Digestion of Casein by Pepsin Hydrochloric Acid and by Pancreas-ferment. EMIL FISCHER and EMIL ABDERHALDEN (*Zeit. physiol. Chem.*, 1903, 45, 215—219. Compare Abstr., 1903, ii, 666).—In addition to the polypeptide previously mentioned, small amounts of α -pyrrolidinecarboxylic acid are also formed by the prolonged action of pepsin hydrochloric acid or of pancreatin on casein. Its formation has been proved by its isolation without the aid of the esterification method. The best yield is obtained when the proteid is first digested

with the pepsin solution and then for some time with pancreatin. Phenylalanine is also formed. The polypeptide has an alkaline action; its alkaline solution gives a reddish-purple coloration with a very little dilute cupric sulphate solution; it yields a precipitate with tannin and also with platinic chloride and alcohol. J. J. S.

Variations in the Action of Pepsin on Fibrin in Acid Liquids at 50°. DISDIER (*J. Pharm. Chim.*, 1903, [vi], 18, 594—605).—It is shown that the digestive power of pepsin diminishes with the time during which it is warmed at 50° with hydrochloric acid (containing 1·5 grams per litre) before the fibrin is added. Syntonisation and peptonisation are found to be most rapid with the 1·5 acid, the former process being, however, equally so with strengths from 1·5 to 2·5 grams per litre. Similar results are obtained with pepsins of an acidic character.

The strengths of hydrobromic, nitric, and sulphuric acids most favourable to the digestive process are found to be almost exactly those equivalent to the 1·5 hydrochloric acid, whilst lactic, oxalic, and formic acids give results different to those obtained with the mineral acids. G. D. L.

Hydrolysis of Edestin. EMIL ABDERHALDEN (*Zeit. physiol. Chem.*, 1903, 249—250. Compare Abstr., 1903, i, 588).—The crude leucine obtained from edestin has been found to contain aminovaleric acid.

J. J. S.

Salmin. ALBRECHT KOSSEL (*Zeit. physiol. Chem.*, 1903, 45, 311—315. Compare Abstr., 1898, i, 714; 1899, i, 833; 1903, i, 303).—Active α -pyrrolidinecarboxylic acid is one of the products obtained by the hydrolysis of salmin with sulphuric acid. The phenylhydantoic acid melted at 137—138°, whereas Fischer (Abstr., 1901, i, 781) gives 143°.

J. J. S.

A Phosphorised Constituent of Plant-seeds. ERNST SCHULZE and ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1903, 40, 120—122).—The compound previously obtained (Abstr., 1896, i, 516) from the seeds of *Sinapis niger* and other seeds is probably a mixture of Posternak's anhydroxymethylene-phosphoric acid (Abstr., 1903, ii, 680) and some other compound richer in carbon.

J. J. S.

The Coagulation of Starch. JULES WOLFF and AUGUSTE FERNBACH (*Compt. rend.*, 1903, 137, 718—719).—Many cereal grains and leaves contain an enzyme, *amylcoagulase*, which precipitates soluble starch from its solutions. A solution containing 4 to 4·5 per cent. of starch is precipitated by a cold water extract of malt. In more dilute solutions, coagulation may not take place, owing to the antagonistic action of amylase, which, however, is more retarded by the addition of sodium hydroxide than is that of *amylcoagulase*. The addition of 0·0001 part of acetic acid or sodium hydroxide prevents the reaction, which also disappears after heating the extract at 65° for five minutes.

The coagulative action is not due to the reversed action of an amylolytic ferment, and it is possible that many assumed cases of

reversible enzyme action (compare Croft Hill, Trans., 1903, 83, 578) may be explicable by the existence of two antagonistic enzymes.

C. H. D.

Enzyme from *Monilia Candida* and a Milk Sugar Enzyme. EDUARD BUCHNER and JAKOB MEISENHEIMER (*Zeit. physiol. Chem.*, 1903, 45, 167—175).—When the method used for the extraction of zymase from yeast is applied to *Monilia candida*, an extract is obtained which has strong inverting properties but does not readily induce alcoholic fermentation. A similar preparation may be obtained by treating the organism with acetone (compare Albert, Abstr., 1901, i, 180; 1902, ii, 521). These preparations presumably contain an enzyme resembling zymase. This *monilia-invertase* will not dialyse through parchment paper, may be mixed for a short time with acetone or ether without being destroyed, and will withstand a temperature of 33° for some time, but appears to lose its activity when strongly diluted with water.

The milk sugar yeast from Armenian Mazun also yields an extract which is capable of inducing slight fermentation in a solution of dextrose or milk sugar, owing probably to the presence of a small amount of a zymase in addition to the lactase. The enzymes zymase, *monilia-invertase*, and yeast lactase resemble one another in certain respects. They only act in the interior of the organism in which they are contained. They can be extracted by the usual method and also remain when the organisms are destroyed by acetone.

J. J. S

Influence of Concentrated Sugar Solutions on Yeast Invertase. THOMAS BOKORNY (*Chem. Zeit.*, 1903, 27, 1106—1107. Compare Abstr., 1902, i, 848).—The observation made by the author that a syrupy solution of sucrose is not so readily fermented as a similar solution of dextrose led to the conclusion that invertase is affected by concentrated sugar solutions, and to a greater degree than zymase. Invertase in expressed yeast is stable up to 35—40°. The action of invertase on sucrose is very rapid; for instance, a 5 per cent. sugar solution, to which the requisite amount of expressed yeast has been added, reduces Fehling's solution after a few minutes.

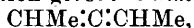
Experiments are quoted on the action of expressed yeast on sucrose and dextrose solutions of varying concentrations. The invertase ceases to act on the sucrose solutions when a certain concentration has been reached, whilst the zymase is not affected to the same extent by the increasing concentration of dextrose.

A. McK.

Organic Chemistry.

Preparation and Properties of Symmetrical Dimethylallene.

CONSTANT KUKURITSCHKIN (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 873—882).—The action of phosphorus pentachloride on trichloroamyl alcohol yields: (1) a *trichloropentylene*, $C_5H_7Cl_3$, to be investigated later, and (2) $\beta\gamma\delta$ -tetrachloropentane. Treatment of the latter with zinc dust in alcoholic solution gives: *s*-dimethylallene,



which boils at 49—51° and has the sp. gr. 0.7217 at 0°/0° and 0.7024 at 20°/0°. It does not react with an ammoniacal solution of cuprous chloride or with alcoholic silver nitrate. When treated in ethereal solution with sodium, it gives a compound which, when carbon dioxide is passed through the solution, yields Δ^a -hexinoic acid: (1) $3CHMe:C:CHMe + 2Na = 2CH_3 \cdot CH_2 \cdot CH_2 \cdot C:CNa + C_5H_{10}$ and (2) $CH_3 \cdot CH_2 \cdot CH_2 \cdot C:CNa + CO_2 = CH_3 \cdot CH_2 \cdot CH_2 \cdot C:CO_2Na$. With alcoholic potassium hydroxide, it gives Δ^b -pentinene, thus: (1) $CHMe:C:CHMe + EtOH = CH_3Me \cdot C(OEt):CHMe$; (2) this compound then breaks down giving $EtOH + CEt:CMc$. T. H. P.

Preparation of Primary Alcohols from the Corresponding Amides. LÉON BOUVEAULT and GEORGES BLANC (*Compt. rend.*, 1904, 138, 148—150).—A solution, made by dissolving the amide in three times its weight of ethyl alcohol, is allowed to flow on to sodium (6 atoms) placed in a flask provided with a long condenser. After the violent reaction is over, the mixture is heated until all the sodium has dissolved. Water is then added and the whole distilled in steam; the mixture of the amine and corresponding alcohol which passes over can be separated by means of acid. The amides of *n*-hexoic, *n*-nonoic, and phenylacetic acids, when subjected to this treatment, furnished *n*-hexyl and *n*-nonyl alcohols and benzylcarbinol respectively. The yields vary between 25 and 30 per cent. of the theoretical. S. S.

A New Method of Synthesising Tertiary Alcohols with Organomagnesium Compounds. VICTOR GRIGNARD (*Compt. rend.*, 1904, 138, 152—154).—When compounds of the type $R \cdot CO \cdot O \cdot MgX$ are warmed with a magnesium alkyl haloid, the following reactions take place: $RCO \cdot OMgX + R'MgX = CRR'(OMgX)_2$, $CRR'(OMgX)_2 + R'MgX = CRR'_2 \cdot OMgX + O(MgX)_2$. By decomposing the product with ice, acidifying, and extracting with ether, a tertiary alcohol can be isolated in good yield. The following new alcohols were prepared by this method. *Diethylisoamylcarbinol*, a mobile liquid of agreeable odour, boiling at 83—86° under 15 mm pressure, having the sp. gr. 0.852 at 0°, 0.844 at 10.4°/4°, and $n_D = 1.44092$; the *acetate* boils at 93—94° under 14 mm. pressure. *isoButyldiisoamylcarbinol* is an oily liquid which boils at 126—129° under 15 mm. pressure, has the

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sp. gr. 0.8498 at 0°, 0.8416 at 10.4°/4°, and n_D 1.44864. *Phenyl-diethylcarbinol*, a mobile liquid which boils at 101—102° under 11 mm. pressure, has the sp. gr. 1.0029 at 0°, 0.9936 at 11°/4°, and n_D = 1.52672. S. S.

Addition of Hypochlorous Acid to Allene Hydrocarbons. I. F. W. SMIRNOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 854—872).—When two molecules of hypochlorous acid combine with one of allene or of an unsymmetrically substituted allene, the chief products are chlorinated keto-alcohols, which have distinctive properties and may be employed for characterising the allene hydrocarbons.

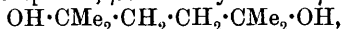
Chloroacetylcarbinol (α -hydroxy- γ -chloroacetone), $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH}$, obtained in about 40—50 per cent. yield by the action of hypochlorous acid on allene, separates from alcohol in crystals melting at 74—75°; it is readily decomposable and, at its melting point, evolves hydrogen chloride; it reduces Fehling's solution at the ordinary temperature, gives a crystalline compound with sodium hydrogen sulphite, and yields the corresponding acetyl compound with acetic anhydride; the action of hydroxylamine on its decomposition products gives methylglyoxime. Other compounds obtained by the action of hypochlorous acid on allene are s -dichloroacetone, β -chloroallyl alcohol, and $\beta\beta$ -dichloropropylene glycol.

The action of hypochlorous acid on allene hence takes place in the following different ways: (1) $\text{CH}_2\text{:C:CH}_2 + \text{HClO} = \text{CH}_2\text{:CCl}\cdot\text{CH}_2\cdot\text{OH}$, and then (a) $\text{CH}_2\text{:CCl}\cdot\text{CH}_2\cdot\text{OH} + \text{HClO} = \text{CH}_2\text{Cl}\cdot\text{CCl}(\text{OH})\cdot\text{CH}_2\cdot\text{OH} = \text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH} + \text{HCl}$ and (b) $\text{CH}_2\text{:CCl}\cdot\text{CH}_2\cdot\text{OH} + \text{HClO} = \text{OH}\cdot\text{CH}_2\cdot\text{CCl}_2\cdot\text{CH}_2\cdot\text{OH}$, (2) $\text{CH}_2\text{:C:CH}_2 + 2\text{HClO} = \text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{CH}_2\text{Cl} + \text{H}_2\text{O}$.

The dichloropropylene glycol is formed only in very small amount.

T. H. P.

Transformations of Octyl ditert- γ -Glycol (γ -Tetramethylbutyleneglycol). S. POGORZELSKY (*J. Russ. Phys. Chem. Soc.*, 882—896).—This compound, $\beta\epsilon$ -dimethylhexane- $\beta\epsilon$ -diol,



previously obtained by Zelinsky (*Abstr.*, 1902, i, 593), was prepared by the action of magnesium methiodide on ethyl succinate and is found to melt at 88.5—89° and not at 92—93° as stated by Zelinsky (*loc. cit.*).

The action of aqueous sulphuric acid (of strengths varying from 10 per cent. acid to a mixture of 3 vols. of acid and 2 of water) on the glycol yields the corresponding oxide, $\begin{matrix} \text{CH}_2\cdot\text{CMe}_2 \\ | \\ \text{CH}_2\cdot\text{CMe}_2 \end{matrix} > \text{O}$, which is also obtained

by the action of hydrochloric acid on the glycol. By treating the glycol with acetic acid at temperatures up to 100°, the monoacetyl derivative is obtained together with a small proportion of the diacetyl compound; but with concentrated acetic acid in a sealed tube at 125° the glycol yields this oxide. In all cases it is supposed that with acetic acid the monoacetyl derivative is obtained, but that at higher temperatures (above 100°), this splits up into the oxide and acetic acid; probably a

similar action takes place when the glycol is heated with sulphuric or hydrochloric acid. The glycol is not acted on by aqueous potassium hydroxide, either at the ordinary temperature or when heated in a water-bath.

The action of potassium hydroxide solution on diisocrotyl bromide varies with the temperature. In all cases, however, the first change is the same, namely: $\text{CMe}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}_2\text{Br} + \text{H}_2\text{O} = \text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}_2\text{Br} + \text{HBr}$. If the temperature is higher than 77° , the compound thus formed splits up giving the corresponding oxide and hydrogen bromide, whilst at lower temperatures it takes up water and gives the glycol and hydrogen bromide. T. H. P.

Etherates of Haloid Compounds of Magnesium. BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 610—623).—The author has determined the solubilities in ether at different temperatures of the compounds $\text{MgBr}_2\cdot 2\text{Et}_2\text{O}$ and $\text{MgI}_2\cdot 2\text{Et}_2\text{O}$ (see Tissier and Grignard, *Abstr.*, 1901, i, 316; and Zelinsky, *Abstr.*, 1903, i, 802), to which he gives the name of “dietherates.” Two non-miscible liquid layers are formed, from the lower of which the dietherate is obtained on cooling. The dietherate of magnesium bromide melts under ether at $22\cdot 8^\circ$. Complete miscibility of the two layers of liquid was found to be unattainable, owing to decomposition occurring before a sufficiently high temperature was reached. This dietherate may melt under ether at higher temperatures than $22\cdot 8^\circ$. For this to take place, it is necessary that the quantity of ether in contact with the solid dietherate be less than is contained in the lower liquid layer at $22\cdot 8^\circ$. The content of dietherate in the solution then increases to 85·5 per cent. at 30° , but with greater concentrations, that is, when still less ether is taken, the dietherate decomposes into monoetherate and ether.

With the magnesium iodide compound, two liquid layers are obtained with ether, the melting point of the compound under ether being $23\cdot 6^\circ$; the critical solution temperature is $38\cdot 5^\circ$. The pure magnesium iodide dietherate melts at $51\cdot 5^\circ$. T. H. P.

The Phosphoric Esters of Glycerol. P. CARRÉ (*Compt. rend.*, 1904, 138, 47—49. Compare this vol., i, 133).—A description of the properties of the three glyceryl phosphates which are obtained by the action of glycerol on phosphoric acid. Glyceryl dihydrogen phosphate (glycerophosphoric acid), $\text{PO}(\text{OH})_2\cdot\text{O}\cdot\text{C}_3\text{H}_5(\text{OH})_2$, is best obtained by decomposing an aqueous suspension of the lead salt with hydrogen sulphide, and concentrating the filtrate from the lead sulphide under reduced pressure; it forms an uncrystallisable syrup. It is impossible to obtain it quite pure and free from water, for, at a certain concentration (2 mols. acid, 1 mol. water), it begins to change to the diposphate. Glyceryl hydrogen phosphate, $\text{OH}\cdot\text{PO}\begin{smallmatrix} \text{O}\cdot\text{CH}_2 \\ \text{O}\cdot\text{CH}_2 \end{smallmatrix} \text{CH}\cdot\text{OH}$, was not isolated; in aqueous solution, it readily decomposes giving the monophosphate. Glyceryl phosphate, $\text{PO}\cdot\text{O}_3\cdot\text{C}_3\text{H}_5$, was obtained as a spongy mass, insoluble in water and alcohol. S. S.

Esterification by means of Sulphuric Acid. HANS MEYER (*Monatsh.*, 1903, 24, 840—843).—In the ordinary method of esterification by means of sulphuric acid, an excess of alcohol is employed, and only the minimum quantity of mineral acid is added. It is often advantageous to dissolve the acid in concentrated sulphuric acid and to add an equivalent quantity of the alcohol. After stirring, the solution is poured on to crystallised sodium carbonate, neutralisation thus occurring without development of heat. Mixed anhydrides or acylsulphuric acids, $R \cdot CO \cdot SO_4H$, are first formed and then react with the alcohol forming the ester. The method gives good results with acids of the pyridine series and with most fatty and aromatic acids. No esterification occurs in the case of *p*-hydroxybenzoic acid or terephthalic acid, the *p*-substituent apparently hindering the formation of acylsulphuric acids (compare Abstr., 1901, i, 628).

C. H. D.

The Theory of Saponification. LUIGI BALBIANO (*Ber.*, 1904, 37, 155—157. Compare Abstr., 1903, i, 547, and Lewkowitsch, this vol., i, 6).—In the benzylation of glycerol by Baumann's method, the product, even when only a few drops of benzoyl chloride have been added, is pure tribenzoin; the esterification, therefore, takes place in the three hydroxyl groups simultaneously and not in stages.

C. H. D.

Salts of Antimony with Organic Acids. I. EDUARD JORDIS (*Zeit. angew. Chem.*, 1904, 17, 41—45. Compare Abstr., 1902, i, 740; 1903, ii, 603).—A theoretical paper.

A. McK.

α -Iodopropionic Acid. WLADIMIR ZERNOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 962—964).— α -Iodopropionic acid, which has previously been obtained only in the form of an impure, non-crystallisable syrup, may be prepared (1) by heating propionic acid (1 mol.), phosphorus pentachloride ($1\frac{1}{4}$ mols.), and chloroform (2 mols.) together at 65°, and gradually adding iodine chloride until the colour of iodine appears in the liquid, the products of the reaction being then decomposed by means of ice-cold water and shaken with sodium carbonate solution; after removal of the chloroform, an oil remains which solidifies in the desiccator to acicular crystals, melting, after recrystallisation from light petroleum, at 44·5—45·5°. (2) By treating ethyl α -bromopropionate in alcoholic solution with potassium iodide and hydrolysing the ester thus obtained with cold barium hydroxide solution. The acid is readily soluble in most organic solvents, but only slightly so in light petroleum or water. Its *lithium* ($+H_2O$), *magnesium* ($+4\frac{1}{2}H_2O$), *barium* and *copper* salts were prepared. Most of its salts are extremely readily soluble in water.

T. H. P.

Action of Nitrogen Peroxide on Acids of the Series $C_nH_{2n-2}O_2$. IV. Action of Nitrogen Peroxide on Allylacetic Acid, its Ethyl Ester, and on Propylideneacetic Acid and its Ethyl Ester. IWAN W. EGOROFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 965—973. Compare Abstr., 1903, i, 789 and 790).—The

action of nitrogen peroxide on an ice-cold light petroleum solution of ethyl allylacetate yields a yellow oil which analysis and cryoscopic examination show to be a mixture of mononitro-derivative, $C_7H_{12}O_2(NO_2) \cdot OH$, and the dinitro-compound, $C_7H_{12}N_2O_6$. The oil is soluble in alkali, to which it imparts a red colour, and on heating it decomposes with evolution of brown vapours. Reduction with tin and hydrochloric acid yields a product from which platinic chloride separates the *platinichloride* of *ethyl γ -diaminovaleate*,



With allylacetic acid, under similar conditions, a small quantity of succinic acid is obtained, together with a mixture of the $NO_2 \cdot ONO$ and $NO_2 \cdot OH$ compounds, and possibly also the $NO_2 \cdot NO_2$ derivative. Reduction of this mixture with tin and hydrochloric acid and treatment of the resulting product with platinic chloride gives the *platinichloride* of *γ -diaminovaleic acid*, $NH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CH_2 \cdot CH_2 \cdot CO_2H, H_2PtCl_6$.

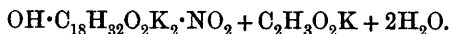
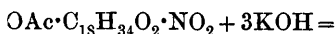
Free diaminovaleic acid could only be obtained in small quantity from its compound with phosphotungstic acid. Aminovaleic acid, which is also probably formed in the above reduction, could not be separated.

Treatment of propylideneacetic acid and its ethyl ester with nitrogen peroxide yields corresponding mixtures of dinitro- and hydroxy-nitro-derivatives, which gradually decompose with separation of oxalic and propionic acids. Reduction with tin and hydrochloric acid yields a *hydroxyamino-acid*, $OH \cdot C_5H_8O_2 \cdot NH_2$, which separates in crystals containing H_2O and melting at about 125° . T. H. P.

Action of Nitrogen Peroxide on Acids of the Series $C_nH_{2n-2}O_2$.

V. Action of Nitrogen Peroxide on Oleic and Elaidic Acids. IWAN W. EGOBOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 973—997. Compare Abstr., 1903, i, 789 and 790, and preceding abstract).—It was shown by Varrentrapp (*Annalen*, 1840, 35, 196) and by Hermann Meyer (*Annalen*, 1840, 35) that nitrous acid gives additive products with oleic acid, and also converts it into elaidic acid. Lidoff (*J. Russ. Phys. Chem. Soc.*, 1895, 27, 117) found that nitrogen peroxide in the cold converts oleic acid into its isomeride, whilst at 80 — 85° it forms additive products.

The author finds that small quantities of nitrogen peroxide act on oleic acid giving an additive product, and it is only when this latter is present in a certain proportion, for the formation of which a certain minimum quantity of nitrogen peroxide is required, that the isomeric change of oleic into elaidic acid can take place. The action of still larger quantities of nitrogen peroxide on an ice-cold light petroleum solution of oleic acid yields: (1) a crystalline product which proves to be the *nitrous ester* of *nitrohydroxystearic acid*, $NO_2 \cdot C_{18}H_{34}O_2 \cdot O \cdot NO$, and which crystallises from alcohol in large, thin plates melting at 85 — 87° , and soluble in ether or ethyl acetate; it has the normal molecular weight in freezing acetic acid, and on keeping it gives up nitrogen and oxygen. With acetic anhydride, it gives the *acetyl* derivative of *nitrohydroxystearic acid*, $OAc \cdot C_{18}H_{34}O_2 \cdot NO_2$, as a pale yellow oil, which, when treated with potassium hydroxide, yields nitrohydroxystearic acid,



(2) Nitrohydroxystearic acid, in the form of a yellow oil. Reduction of the mixed products of the action of nitrogen peroxide on oleic acid by means of zinc and hydrochloric acid yields stearic acid and its mono- and di-hydroxy-derivatives, together with the hydrochloride of an *aminohydroxystearic acid*, $\text{OH} \cdot \text{C}_{18}\text{H}_{34}\text{O}_2 \cdot \text{NH}_2 \cdot \text{HCl}$, which crystallises in needles melting at $143-144^\circ$; the *barium* salt, $(\text{C}_{18}\text{H}_{35}\text{O}_2)_2\text{Ba}$, of this acid was prepared, but the acid separated from it did not give concordant numbers on analysis.

The action of nitrogen peroxide on olive oil yields a mixture of the glycerides of nitrohydroxystearic acid and of its nitrous ester; treatment of this mixture with acetic anhydride gives the glyceride of nitroacetoxystearic acid, $[\text{C}_{18}\text{H}_{33}\text{O}_2(\text{NO}_2) \cdot \text{OAc}]_3\text{C}_3\text{H}_5$, in an almost pure condition.

The author sums up the results of his previous researches (*loc. cit.*) and of the present work and draws from them the following conclusions: (1) the first product of the action of nitrogen peroxide on an acid of the series $\text{C}_n\text{H}_{2n-2}\text{O}_2$ is a compound of the composition $\text{NO}_2 \cdot \text{C}_n\text{H}_{2n-2}\text{O}_2 \cdot \text{O} \cdot \text{NO}$; only when the double linking is far removed from the carboxyl group, and when the molecule contains the grouping, $\text{CH}_2 \cdot \text{C} <$, is the formation of a certain quantity of the compound $\text{C}_n\text{H}_{2n-2}\text{O}_2(\text{NO}_2)_2$ possible. (2) The action of nitrogen peroxide on esters and glycerides of acids of the series $\text{C}_n\text{H}_{2n-2}\text{O}_2$ is similar to its action on the free acids. (3) It is probable that, when left in the air in presence of moisture, the compound $\text{NO}_2 \cdot \text{C}_n\text{H}_{2n-2}\text{O}_2 \cdot \text{O} \cdot \text{NO}$ passes into $\text{OH} \cdot \text{C}_n\text{H}_{2n-2}\text{O}_2 \cdot \text{NO}_2$. (4) The method of combination of the groups ONO and NO_2 with the acids $\text{C}_n\text{H}_{2n-2}\text{O}_2$ is similar to that of hydriodic acid with these acids, NO_2 taking the place of iodine, and ONO that of hydrogen. (5) The spontaneous decomposition of the products of the combination of nitrogen peroxide with the unsaturated acids, $\text{C}_n\text{H}_{2n-2}\text{O}_2$, may be used as a means of determining the position of the double linking in the acid. (6) Although the products of the action of nitrogen peroxide on *isocrotonic* acid are identical with those obtained from *crotonic* acid and the products from *oleic* identical with those from *elaidic* acid, the successive steps in the reaction are different in the two cases. (7) The conversion of *oleic* into *elaidic* acid requires the presence of a certain minimum quantity of nitrogen peroxide, and is accompanied by the formation of additive products. T. H. P.

aa-Dialkylhydracrylic Acids. EDMOND E. BLAISE and L. MARCILLY (*Bull. Soc. chim.*, 1904, [iii], 31, 110-119. Compare Abstr., 1902, i, 357, and succeeding abstract).—Ethyl bromoisobutyrate (40 grams), dry trioxymethylene (14 grams), zinc filings (35 grams), and dry benzene (120 grams) were mixed together and after vigorous action had ceased a further 40 grams of the bromo-ester were added, and the mixture heated on the water-bath for 30 minutes. The product was freed from dissolved zinc and unchanged trioxymethylene by pouring into excess of water, and agitation of the solution of the reaction products in benzene first with dilute sulphuric acid and then with ammonia. The products of the reaction were separated into

three volatile fractions and a non-volatile residue. The first fraction boiled at 84—86° under 16 mm. pressure, and when hydrolysed with potassium hydroxide, dissolved in alcohol, furnished β -hydroxy- $\alpha\alpha$ -dimethylpropionic acid (compare succeeding abstract), but when treated with potassium hydroxide dissolved in water there was formed, in addition to the foregoing acid, diisopropyl ketone (the *semicarbazone* crystallises in spangles and melts at 150—151°), whence it was concluded that the first fraction contained ethyl hydroxydimethylpropionate (Abstr., 1902, i, 357) and ethyl isobutyrylbutyrate.

The second fraction, which boiled at 110—116° under 18 mm. pressure, consisted principally of ethyl tetramethylsuccinate (compare Brown and Walker, Abstr., 1893, i, 394). The third fraction boiled from 151—160° under 15 mm. pressure and consisted of β -hydroxy- $\alpha\alpha\gamma\gamma$ -tetramethylglutarate (Abstr., 1898, i, 631).
T. A. H.

Hydroxypivalic Acid [β -Hydroxy- $\alpha\alpha$ -dimethylpropionic Acid]. L. MARCILLY (*Bull. Soc. chim.*, 1904, [iii], 119—130).—[β -Hydroxy- $\alpha\alpha$ -dimethylpropionic acid], $\text{OH}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$, prepared as described in the preceding abstract, crystallises in clear needles, melts at 124°, is very soluble in water, alcohol, or benzene, less so in ether, and insoluble in light petroleum. Its electric conductivity K is 0.00139, which is slightly higher than that of pivalic acid, —0.000978. When oxidised by chromic acid in presence of sulphuric acid, it is converted into dimethylmalonic acid. The *calcium*, *sodium*, *ammonium*, and *copper* salts are described. The ethyl ester (Abstr., 1902, i, 357) is a colourless liquid with a pleasant odour; it boils at 133° under 40 mm. and at 188° under 750 mm. pressure and has a sp. gr. 0.9985 at 20°/4°. The *methyl* ester boils at 177—178° under 740 mm. pressure and has a sp. gr. 1.0365 at 20°/4°. No amide, anilide, or *p*-toluidide of the acid could be obtained.

Benzylamine hydroxydimethylpropionate crystallises in needles and melts at 108—109°, and, when heated at 200—220° for 3 hours, is converted into the corresponding *benzylamide*; this crystallises in transparent tablets, melts at 64°, and is insoluble in light petroleum. The *phenylhydrazide*, similarly prepared, crystallises from ethyl acetate in yellow-tinted spangles, melts at 173°, and is insoluble in water.

Ethyl β -acetoxydimethylpropionate, $\text{OAc}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$, prepared by acetylating ethyl hydroxypivalate with acetyl chloride, is a liquid of pleasant odour, boils at 94° under 16 mm. pressure, at 202° under 750 mm., and has a sp. gr. 1.0100 at 20°/4°. The *methyl* ester boils at 191—192° under 737 mm. pressure and has a sp. gr. 1.0338 at 20°/4°. The free acid crystallises from light petroleum, melts at 56°, and is very soluble in alcohol. The *calcium* salt was prepared.

When ethyl hydroxydimethylpropionate, dissolved in ether, is treated with metallic sodium and ethyl iodide, a mixture of two esters is formed. The more volatile of these consists of *ethyl ethoxydimethylpropionate*, a pleasant-smelling liquid which boils at 75° under 22 mm. pressure, and, on hydrolysis, furnishes β -ethoxy- $\alpha\alpha$ -dimethylpropionic acid, which is crystalline and boils at 123° under 22 mm. pressure. The *sodium* salt of this was prepared.

The less volatile ester consists of *ethyl hydroxydimethylpropionyl-*

oxydimethylpropionate, $\text{OH} \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{CO} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{CO}_2\text{Et}$, which distils at 154° under 27 mm. pressure, and, when hydrolysed by potassium hydroxide dissolved in alcohol, furnishes hydroxypivalic acid.

With phenylcarbimide, hydroxydimethylpropionic acid furnishes the corresponding *phenylurethane*, $\text{NPh} \cdot \text{CO} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$, which crystallises from light petroleum or boiling water and melts at 126° . The *potassium* salt of this is crystalline, melts at $129-130^\circ$, and is very soluble in water. T. A. H.

Researches in the Glyceric Acid Series. I. *d*- and *l*-Glyceric Acids. CARL NEUBERG and M. SILBERMANN (*Ber.*, 1904, 37, 339—341).—In a research not yet published, Neuberg and Neimann obtained from *d*-glucuronic acid an optically active glyceric acid, the barium salt of which had $[\alpha]_D + 17.1^\circ$. Frankland and Appleyard (*Trans.*, 1893, 63, 298) find $[\alpha]_D - 10.1^\circ$ for the barium salt of the *d*-acid, obtained by the growth of *Bacillus ethaceticus* on calcium *i*-glycerate. The authors have accordingly resolved *i*-glyceric acid into its optically active components by means of brucine, the solvent being ethyl alcohol. The brucine salt, obtained after four crystallisations, was decomposed by baryta water, and the resulting barium salt gave $[\alpha]_D - 17.38^\circ$ ($c = 7.704$) in aqueous solution. The mother liquor, from which the brucine *d*-glycerate had been separated, yielded a barium salt having $[\alpha]_D 8.75^\circ$ ($c = 13.71$). A. McK.

Researches in the Glyceric Acid Series. II. Conversion of Diaminopropionic Acid into *iso*Serine. CARL NEUBERG and M. SILBERMANN (*Ber.*, 1904, 37, 341—345. Compare preceding abstract and Ellinger, this vol., i, 230).—The transformations undergone by amino-acids are important in connection with the formation of sugars from proteids. Neuberg and Wolff (*Abstr.*, 1903, i, 74) have already shown that *d*- α -amino-*n*-hexoic acid can be obtained from *d*-glucosaminic acid. The replacement of the amino-groupings in $\alpha\beta$ -diaminopropionic acid has now been studied.

*iso*Serine was produced by the action of silver nitrite on $\alpha\beta$ -diaminopropionic monohydrobromide; it was identified by its copper and phenylcarbimide derivatives (E. Fischer and Leuchs, *Abstr.*, 1903, i, 12).

The *phenylcarbimide* derivative of $\alpha\beta$ -diaminopropionic acid, prepared from $\alpha\beta$ -diaminopropionic hydrochloride, sodium hydroxide solution, and phenylcarbimide, melts and decomposes at 214° (corr.).

A. McK.

Separation of Hydrogen Ions from Methylene Groups. RICHARD EHRENFELD (*Ber.*, 1904, 34, 83—84).—A reply to Wagner and Hildebrandt's criticisms (this vol., i, 140). W. A. D.

Cryoscopic Observations on Solutions of Oxalic Acid in presence of Neutral Salts. A. FEDOROFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 643—644).—The author has made cryoscopic measurements of (1) solutions of oxalic acid, ammonium chloride, and ammonium oxalate, containing from one-half to one-thirty-second of an

equivalent per litre, and (2) solutions of oxalic acid mixed with those of either ammonium chloride or ammonium oxalate. The first of these salts does not affect the cryoscopic behaviour of oxalic acid, but, when the latter is present, depressions less than the normal are obtained. This the author considers to be due to the formation of acid or complex salts.

T. H. P.

Coefficient of Distribution of Oxalic Acid between Water and Ether in presence of Neutral Salts. A. FEDOROFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 639—640).—The concentration of the oxalic acid in the aqueous phase is increased by the addition of sodium or potassium oxalate, but diminished in presence of ammonium chloride.

T. H. P.

Asymmetric Synthesis. WILLY MARCKWALD (*Ber.*, 1904, 37, 349—354).—All previous attempts to synthesise an optically active carbon compound, as, for example, Cohen and Whitely (*Proc.*, 1901, 16, 212), Kipping (*Proc.*, 16, 226), and Fischer and Slimmer (*Abstr.*, 1902, i, 621), have been based on the one principle; they have involved the combination of an inactive compound, containing an ethylene linking or a carbonyl group, with an optically active substance to form an ester or glucoside, and the subsequent treatment of this product in such a way as to attach two different groups to a carbon atom previously ethenoid so as to render it asymmetrical. As Japp and others have pointed out, the two possible isomerides should not necessarily be formed in equal quantities, so that one of the isomerides would preponderate on hydrolysing the new ester or glucoside, and therefore an optically active substance should be obtained. The formation in this manner of optically active substances has not yet, however, been conclusively established.

Methylethylmalonic acid, $\text{CMeEt}(\text{CO}_2\text{H})_2$, forms two acid salts, which, in the case of the potassium salt, are enantiomorphously related and will have the same solubility, whereas the two acid salts with an optically active base will in general have different solubilities. When heated, methylethylmalonic acid loses carbon dioxide, forming α -methylbutyric acid, which contains an asymmetric carbon atom; it is to be supposed that from the acid brucine salts the free carboxyl group will be preferentially eliminated. On heating the brucine salt, crystallised from the mixture of the two in an oil-bath at 170° , a valeric acid was obtained which boiled at 174° and in 100 mm. tube showed $\alpha_D - 1.7^\circ$, corresponding with 10 per cent. of active *l*-valeric acid. This, after conversion into its silver salt and reconversion into acid (compare Marckwald, 1899, i, 477), showed a rotation $\alpha_D - 1.2^\circ$ in 50 mm. tube.

E. F. A.

General Method for the Preparation of Aldehydes. ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1904, 37, 186—188. Compare Bouveault, this vol., i, 13; Gattermann and Maffezolli, *ibid.*, 172).—Aldehydes may be synthesised by the action of organomagnesium haloids on the esters of orthoformic acid dissolved in dry ether. The reaction is only completed when the ether has been distilled off, and the acetal thus

obtained, $\text{CH}(\text{OEt})_3 + \text{R} \cdot \text{MgI} = \text{CHR}(\text{OEt})_2 + \text{OEt} \cdot \text{Mg} \cdot \text{I}$, may then be hydrolysed with very dilute acid.

Magnesium ethyl iodide gave a 25 per cent. yield of acetal, magnesium propyl iodide gave 22 per cent. of butaldehyde. The acetal of isovaleraldehyde (80), acetal of benzaldehyde (45), acetal of phenylacetaldehyde (62), *p*-bromobenzaldehyde (40), and anisaldehyde (15 per cent.) have been prepared. J. J. S.

Synthesis of Aldehydes. AUGUSTE BÉHAL and SOMMELET (*Compt. rend.*, 1904, 138, 89—92).—The ethers of α -glycols, corresponding with the formulæ $\text{OH} \cdot \text{CR}_2 \cdot \text{CH}_2 \cdot \text{OX}$ and $\text{OH} \cdot \text{CRR}_1 \cdot \text{CH}_2 \cdot \text{OX}$, in which X represents a univalent alkyl or aromatic residue, are decomposed by heating at 110—115° with dry oxalic acid, yielding substituted aldehydes of the type $\text{CR}_2\text{H} \cdot \text{CHO}$ and $\text{CRR}_1\text{H} \cdot \text{CHO}$, the following scheme representing the probable course of the reaction: $\text{OH} \cdot \text{CR}_2 \cdot \text{CH}_2 \cdot \text{OX} \rightarrow \text{CR}_2 \cdot \text{CH}_2 \cdot \text{OX} \rightarrow \text{CR}_2 \cdot \text{CH}_2 \cdot \text{OH} \rightarrow \text{CR}_2\text{H} \cdot \text{CHO}$.

The α -glycol ethers required for the preparation of the aldehydes, $\text{CR}_2\text{H} \cdot \text{CHO}$, were obtained by Grignard's method (compare Abstr., 1901, i, 250) by the action of ethyl ethoxyacetate on the organomagnesium derivatives, and the following ethers and aldehydes were prepared: *dimethylethoxymethylcarbinol*, which boils at 129°; *diethylethoxymethylcarbinol*, which boils at 168° and yields *α -ethylbutaldehyde*, which boils at 117—118°; *dipropylethoxymethylcarbinol*, which boils at 201° and yields *α -propylvaleraldehyde*, which boils at 159—161°; *diisobutylethoxymethylcarbinol*, which boils at 112—113° under 23 mm. pressure and yields *α -isobutylisohexaldehyde*, boiling at 185—186°; *diisoamylethoxymethylcarbinol*, which boils at 143—144° under 25 mm. pressure and yields *α -isoamylisohexaldehyde*, which boils at 103—105° under 11 mm. pressure; *diallylethoxymethylcarbinol*, which boils at 101—102° under 25 mm. pressure; *diphenylethoxymethylcarbinol*, which boils at 209—210° under 29 mm. pressure and yields *diphenylacetaldehyde*, which boils at 168—170° under 10 mm. pressure; *diethylphenoxymethylcarbinol* boils at 140—142° under 12 mm. pressure and yields *α -ethylbutaldehyde* when heated with dry oxalic acid.

The α -glycol ethers, required for the formation of the aldehydes, $\text{CRR}_1\text{H} \cdot \text{CHO}$, were obtained by the action of organomagnesium compounds on the ketones $\text{R} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{OEt}$, which were prepared by Blaise's method (compare Abstr., 1901, i, 133) from cyanoethoxymethane, $\text{OEt} \cdot \text{CH}_2 \cdot \text{CN}$, and the following compounds were prepared. (1) Ketones: *ethoxybutanone*, which boils at 145—146°; *ethoxypentanone*, which boils at 164—165°; *ethoxymethylhexanone*, which boils at 92—93° under 18 mm. pressure, and *ω -ethoxyacetophenone*, which boils at 134—136° under 21 mm. pressure. (2) α -Glycol ethers: *α -ethoxy- β -ethylpentan- β -ol*, which boils at 180—184°; *α -ethoxy- ϵ -methyl- β -propylhexan- β -ol*, which boils at 109—113° under 12 mm. pressure; *α -ethoxy- β -methyloctan- β -ol*, which boils at 110—112° under 14 mm. pressure; *α -ethoxy- β -methylnonan- β -ol*, which boils at 130—133° under 18 mm. pressure. (3) Aldehydes: *α -ethylvaleraldehyde*, which boils at 141—143°; *α -propylisohexaldehyde*, which boils at 195—198°; *α -methyl-*

octaldehyde, which boils at 92° under 28 mm. pressure, and α -methyl-nonaldehyde, which boils at 98—100° under 20 mm. pressure.

M. A. W.

Compounds of Trichloro- and Tribromo-acetates with Ketones and Aldehydes. L. KOBOSEFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 652—667).—By dissolving trichloroacetates or tribromoacetates in ketones and aldehydes, the following compounds have been obtained. All are crystalline, but do not melt sharply, the temperatures given being those at which melting started when the substances were heated in sealed tubes.

With acetone: $(\text{CCl}_3 \cdot \text{CO}_2)_2\text{HK}, 2\text{COMe}_2$, needles melting at 39°; $(\text{CCl}_3 \cdot \text{CO}_2)_2\text{HK}, \text{COMe}_2$, melting at 56°; $\text{CCl}_3 \cdot \text{CO}_2\text{K}, \text{COMe}_2$, four-sided prisms decomposing without melting; $4(\text{CCl}_3 \cdot \text{CO}_2)_2\text{HNNH}_4, \text{COMe}_2$; $3(\text{CCl}_3 \cdot \text{CO}_2)_2\text{HNNH}_4, \text{COMe}_2$.

With methyl ethyl ketone: $(\text{CCl}_3 \cdot \text{CO}_2)_2\text{HK}, \text{COMeEt}$, melting at 55°.

With pinacolin: $(\text{CCl}_3 \cdot \text{CO}_2)_2\text{HK}, \text{COMe} \cdot \text{CMe}_3$, silky needles melting at 84°; $(\text{CBr}_3 \cdot \text{CO}_2)_2\text{HK}, \text{Me} \cdot \text{CO} \cdot \text{CMe}_3$, decomposing without melting.

With acetylacetone: $(\text{CCl}_3 \cdot \text{CO}_2)_2\text{HK}, \text{COMe} \cdot \text{CH}_2\text{Ac}$, rhombic crystals melting at 52°.

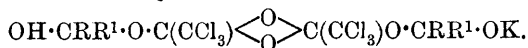
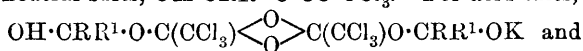
With acetophenone: $(\text{CCl}_3 \cdot \text{CO}_2)_2\text{HK}, \text{COMePh}$, melting at 66°.

With benzaldehyde: $(\text{CCl}_3 \cdot \text{CO}_2)_2\text{HK}, \text{Ph} \cdot \text{CHO}$, melting at 35°; $(\text{CBr}_3 \cdot \text{CO}_2)_2\text{HK}, \text{Ph} \cdot \text{CHO}$, melting at 88·5°.

With salicylaldehyde: $2(\text{CCl}_3 \cdot \text{CO}_2)_2\text{HK}, 3\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$, melting at 41°; $(\text{CCl}_3 \cdot \text{CO}_2)_2\text{HK}, 2\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$, melting at 38°.

Certain other ketones and aldehydes gave negative results.

These compounds readily effloresce in the air and are decomposed by water. The author regards them not as molecular, but structural compounds, and assigns to them the following constitutions: for neutral salts, $\text{OK} \cdot \text{CRR}^1 \cdot \text{O} \cdot \text{CO} \cdot \text{CCl}_3$. For acid salts,



T. H. P.

Synthesis of Glucosides. Derivatives of Arabinose. HUGH RYAN and GEORGE EBRILL (*Sci. Proc. Roy. Irish. Acad.*, 1903, 24, B. 303—386. Compare *Trans.*, 1901, 704).—Crystalline acetochloroarabinose is easily prepared by the action of acetyl chloride on arabinose; it reacts with methyl alcohol, forming the methyl arabinoside melting at 166—168°, previously described by Fischer (*Abstr.*, 1894, i, 3). *Carvacryl arabinoside* crystallises from water in long needles melting at 119—120°; β -*naphthyl arabinoside* forms long, branching, grouped needles from alcohol, melting at 176—177°; *o*-*tolyl arabinoside* crystallises in rosettes melting at 124°. The paper contains a useful summary of previous work on the synthesis of glucosides.

E. F. A.

Some Hydrazones and their Melting Points. A. MÜTHER and BERNHARD TOLLENS (*Ber.*, 1904, 37, 311—315).—*Xylosephenylmethylhydrazone*, $C_5H_{10}O_4 \cdot N_2MePh$, crystallises from very dilute alcohol, melts at 108—110°, is sparingly soluble in water, but dissolves readily in alcohol and in pyridine; the solution in pyridine showed no optical activity.

l-Arabinosephenylmethylhydrazone melts at 164° and not at 161° (van Ekenstein and Lobry de Bruyn); the diphenylhydrazone melts at 203—205° (Neuberg gives 203—206° for inactive *r*-arabinose, but 216—218° for *l*-arabinose), and has $[\alpha]_D + 14.9^\circ$ in pyridine.

A series of experiments showed that Maquenne's metal block for melting point determinations possesses no advantages over the sulphuric acid flask. T. M. L.

***iso*Rhodeose, the Second Methylpentose from Convolvulin.** EMIL VOTOČEK (*Zeit. Zuckerind. Böhm.*, 1904, 28, 209—212. Compare Abstr., 1903, i, 67).—*iso*Rhodeose yields methylfurfuraldehyde on distillation with 12 per cent. hydrochloric acid, and is hence a methylpentose; it has $[\alpha]_D + 20.3^\circ$. Its *phenylosazone* and *p-bromophenylosazone*, melting at 183—184°, were prepared, and the former analysed.

The specific rotations of rhodeose and *isorhodeose* show that the crude syrupy rhodeose consists of a mixture of 1 mol. of rhodeose and 2 mols. of *isorhodeose*. The crude syrup from convolvulin contains also 1 mol. of dextrose. T. H. P.

Synthesis of Sugars from Trioxymethylene and Sodium Sulphite. ALPHONSE SEYEWETZ and GIBELLO (*Compt. rend.*, 1904, 138, 150—152).—Trioxymethylene (1 part) was dissolved in water (200 parts) containing sodium sulphite (20 parts anhydrous salt) and the mixture boiled; at the end of ten minutes, all odour of formaldehyde had vanished, and the osazones of the sugars formed were precipitated by warming with phenylhydrazine acetate. Examination of the crude osazones revealed the presence of formosazone melting at 148°, and glycerosazone which melted at 131°; another substance was isolated, but has not yet been identified. *a*-Acrosazone was absent.

S. S.

The Mutarotation of Sugars. E. ROUX (*Ann. Chim. Phys.*, 1903, [vii], 30, 422—432).—By a modification of Muller's method (compare Abstr., 1894, i, 268), the author has redetermined the velocity of transformation of α - into β -glucose, and extended the investigation to the correlated transformation of γ - into β -glucose; he finds that with a unit of time of 30 minutes the velocity of the conversion of α - into β -glucose is practically independent of the concentration, being 1.315 for a 5 per cent. solution, and 1.345 for a 10 per cent. solution at the same temperature, and further that the conversion of γ - into β -glucose proceeds at about the same rate, the velocity being 1.40 for an 8 per cent. solution at 18°. A mixture of α - and γ -glucoses in the proportion of 36.73 : 63.27 has a specific rotatory power equal to that of the β -variety, exhibits no mutarotation, and behaves in fact

like a *racemic* mixture. Similar results were obtained with α - and γ -lactoses, the velocities of conversion of each of these into the β -variety being 1.334 and 1.305 respectively, and a mixture of the two in the proportion of 36.3 : 63.7 acting as a "*racemic mixture*" and having a constant specific rotation equal to that of β -lactose [compare, however, Lowry, *Trans.*, 1899, 75, 212 ; 1903, 83, 1320].

M. A. W.

Melibiose. D. LOISEAU (*Zeit. Ver. deut. Zucker-Ind.*, 1903, 1050—1061).—The author has made a very complete study of the properties of pure melibiose prepared from raffinose by fermentation with a top yeast. The sugar crystallises with $2\text{H}_2\text{O}$ from aqueous or aqueous alcoholic solutions, and is very soluble in cold water and soluble in all proportions in water at 75° . Crystalline melibiose loses its water of crystallisation completely at 120° and the anhydrous sugar absorbs from the air twice the normal quantity of water, half of which is again given up. When first dissolved, hydrated melibiose has a lower specific rotation than the normal, whilst the anhydrous sugar gives at first a higher value; the ultimate normal rotation is 1.926 compared with that of sucrose as unity. If dissolved in presence of an acid or an alkali, melibiose gives the normal rotation immediately; the addition of lead acetate lowers the rotation considerably, but does not precipitate the melibiose. The sugar is only slightly soluble in alcohol, which, in 95 per cent. strength, only dissolves 2—2.4 parts at 15° . Three to 4 parts of melibiose are required to produce the same sweetening effect as 1 part of sucrose.

T. H. P.

Quantity of Non-fermentable Sugar in Sugar Cane Molasses. HENRI PELLET and G. MEUNIER (*Zeit. Ver. deut. Zucker-Ind.*, 1903, 574, 1182—1185).—Analysis of the molasses from an Egyptian cane-sugar factory gave the following results: H_2O , 26.73; crystallisable sugar, 36.40; dextrose, 6.10; lævulose, 8.48; glucose, 2.40; mannose, 0.20; mineral matter (without CO_2), 8.40, and organic matter, 11.30 per cent. The glucose is quite unfermentable, and so remains in the liquid after fermentation. For the control of the results obtained by the fermentation process, the authors recommend the estimation of the reducing substances before and after inversion by the method given by Pellet (*Bull. de l'Assoc. des Chim. de suc. et de dist.*, 1898—1899, 1006—1145).

T. H. P.

Products of Hydrolysis of Fucus, Laminaria, and Carrageen Moss. A. MÜTHER and BERNHARD TOLLENS (*Ber.*, 1904, 37, 298—305).—Seaweed (fucus) was extracted with cold 2 per cent. sulphuric acid, the extract neutralised with calcium carbonate, evaporated under reduced pressure, partially freed from inorganic salts by precipitating with alcohol, further purified by adding sulphuric acid to convert the inorganic salts into sulphates insoluble in alcohol, and neutralising with lead carbonate and hydrogen sulphide, and finally a syrup was obtained which deposited needle-shaped crystals of feebly lævorotatory

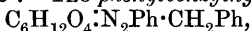
mannitol; this was further characterised by condensing with benzaldehyde to Meunier's tribenzylidenemannitol, a compound which melts at 213—214° and not at 207° as described by Meunier. The residue was then hydrolysed by heating on the water-bath during 8 hours with 5 per cent. sulphuric acid; the extract, neutralised with calcium carbonate and freed from mineral salts by the addition of alcohol, gave a precipitate of fucosephenylhydrazone, which was converted into crystalline fucose. After removing the excess of phenylhydrazine by the addition of formaldehyde, diphenylhydrazine was added and arabinosediphenylhydrazone obtained. The syrupy residue was strongly dextrorotatory and appeared to consist of arabinose with a little fucose. A test for xylose by means of bromine and cadmium carbonate gave a negative result, but the presence of *d*-galactose was proved.

Laminaria, examined by a similar method, gave mannitol, fucose, and glucosazone.

Preliminary experiments with carrageen moss gave indications of glucose, galactose, fructose, and pentose groups. Hydrolysis with 2 per cent. sulphuric acid on the water-bath during 5 hours gave a syrup, from which was precipitated the phenylhydrazone of hydroxymethylfurfuraldehyde, whilst extraction with ethyl acetate gave a yellow liquid which showed five of the characteristic reactions of this aldehyde. This aldehyde is known to be an intermediate product in the hydrolysis of fructose to lævulinic acid, but it was found to be the chief product even when a much gentler method of hydrolysis was employed. *d*-Galactose was separated as methyl- and benzyl-phenylhydrazones and characterised by its rotatory power and by oxidation to mucic acid.

T. M. L.

Fucose and Fuconic Acid and a Comparison with Votoček's Rhodeose and Rhodeonic Acid. A. MÜTHER and BERNHARD TOLLENS (*Ber.*, 1904, 37, 306—311).—*Fucose diphenylhydrazone*, $C_6H_{12}O_4 \cdot N_2Ph_2$, crystallises from 95—96 per cent. alcohol in colourless needles and melts at 198°. The *phenylmethylhydrazone*, $C_6H_{12}O_4 \cdot N_2MePh$, crystallises in colourless needles which melt first at 163—164°, but after repeated crystallisation from dilute alcohol at 177°; it closely resembles the preceding compound, but is more soluble; a solution in pyridine gave $[\alpha]_D + 3.6^\circ$. The *phenylbenzylhydrazone*,



was obtained in yellow flakes melting at 161°, but repeated crystallisation gave a colourless product which melted at 172—173°, had $[\alpha]_D + 9.1^\circ$, and resembled in solubility the preceding compound. Attempts to prepare the osazone by means of phenylhydrazine hydrochloride, sodium acetate, and water, and by means of phenylhydrazine acetate gave only the phenylhydrazone.

Fuconic acid was obtained only in the form of its lactone, which melts at 106—107°, and gave $[\alpha]_D + 71.7^\circ$ and $+78.3^\circ$. The potassium, $C_6H_{11}O_6K \cdot 1\frac{1}{2}H_2O$, barium, $(C_6H_{11}O_6)_2Ba$, strontium, and calcium, $(C_6H_{11}O_6)Ca \cdot 5H_2O$, salts are described. The *phenylhydrazide*, $C_6H_{11}O_5 \cdot N_2H_2Ph$, crystallises from hot water in colourless, four-sided flakes and melts at 203—204°.

The following table shows the similarity between fucose and rhodose and leaves little doubt that they are optical isomerides.

| | Fucose. | Rhodose. |
|---|------------------|------------------|
| $[\alpha]_D$ | -73° to -75° | +73° to +75.2° |
| Phenylosazone, m. p. | 158° to 159° | 176.5° |
| Phenylhydrazone, m. p. | 170° to 172° | 172° |
| Phenylmethylhydrazone, m. p.... | 177° | 174° |
| Phenylbenzylhydrazone, m. p. ... | 172° to 173° | 178° to 179° |
| Diphenylhydrazone, m. p. | 198° | 199° |
| <i>p</i> -Bromophenylhydrazone, m. p... | 181° to 184° | 184° |
| | Fuconic. | Rhodoncic. |
| Lactone, m. p. | 106° to 107° | 105.5° |
| Lactone, $[\alpha]_D$ | +73.0° to +78.3° | -76.3° to -69.4° |

The only outstanding difference is in the osazone, which is still under investigation; in the case of fucose, the crude product melts at 155—156°, but when purified, yields a product melting at 170—172°, which is, however, not the osazone but the phenylhydrazone.

T. M. L.

Optical Activity of Cellulose and its Nitro-derivatives. LÉO VIGNON (*Bull. Soc. chim.*, 1904, [iii], 31, 105—108. Compare Levallois, *Abstr.*, 1884, 1288; 1885, 369 and 500; Béchamp, *Abstr.*, 1885, 237; and Vignon, *Abstr.*, 1903, i, 461, 462).—A nitrated cellulose, the composition of which was similar to that required by the formula $C_{24}H_{31}(NO_2)_9O_{21}$, which was soluble in acetone to the extent of 4.5 per cent. and in a mixture of equal volumes of alcohol and ether to the extent of 1.66 per cent., had $[\alpha]_D +19.3^\circ$ in the former solvent ($c=3.848$ grams in 100 c.c.) and $+21.1^\circ$ when dissolved in a mixture of alcohol and ether ($c=1.4943$ grams in 100 c.c.).

Thiocellulose, prepared by treating cotton cellulose first with an aqueous solution of sodium hydroxide and then with carbon disulphide vapour in the absence of light, when dissolved in water to the extent of 0.998 per cent. exhibited a slight dextrorotation. T. A. H.

Progress of the Technology of Explosives since the Development of Organic Chemistry. WILHELM WILL (*Ber.*, 1904, 37, 268—298).—A lecture delivered before the German Chemical Society.

Reversion [Transformation] of Starch Paste. LÉON MAQUENNE (*Compt. rend.*, 1903, 137, 1266—1268. Compare *Abstr.*, 1903, i, 679; this vol., i, 17).—In view of Boidin's recent paper on amylocoagulase (compare this vol., i, 276), the author publishes the results already obtained on the influence of alkalis on the reversion of starch paste; he finds that potassium carbonate employed in increasing quantities behaves similarly to the acids, first accelerating, then retarding, and finally preventing the reversion into amylocellulose. The reversion of starch paste, prepared only with pure water and the mineral matters

contained in the raw starch or extracted from the glass vessels, is a progressive reaction in which the starch tends to recover a form closely related to that which it possessed in the natural product. Starch paste is therefore to be regarded as a true colloidal substance, and in the absence of all foreign matter it is not impossible that it would remain unchanged for an indefinite period. M. A. W.

Transformation and Coagulation of Starch Paste. LÉON MAQUENNE, AUGUSTE FERNBACH, and JULES WOLFF (*Compt. rend.*, 1904, 138, 49—51. Compare Abstr., 1903, i, 679; this vol., i, 17).—The amylocellulose, formed by the spontaneous transformation of starch jelly, does not give a blue colour with iodine until dissolved in a solution of potassium hydroxide; it is not hydrolysed by amylase, and is thus distinguished from the coagulum formed from starch with malt extract. The following method serves to detect amylocellulose which has been produced by spontaneous coagulation. A sample of the starch paste is hydrolysed with excess of malt extract, 10 c.c. of the product are taken out and mixed with 20—25 drops of potassium hydroxide solution of sp. gr. 1·4, and after the lapse of a few minutes acidified with dilute hydrochloric acid. The production of a blue colour with iodine in this solution proves the presence of amylocellulose in the original sample of starch jelly. The spontaneous coagulation of starch proceeds much more slowly than that produced by the action of malt extract. S. S.

Caramel. V. Decomposition Products of Caramelan. FERDINAND STOLLE (*Zeit. Ver. deut. Zucker-Ind.*, 1903, 1149—1157. Compare Abstr., 1900, i, 209, and ii, 249; 1901, i, 673).—On hydrolysing caramelan with 3 per cent. sulphuric acid solution, the following products were obtained: (1) 14·64 per cent. (on the weight of caramelan) of a chocolate-brown, humous substance, $(C_9H_{11}O_5)_x$, which is insoluble in water, alcohol, acetic acid, or acetone, and on oxidation with nitric acid of sp. gr. 1·15 yields oxalic acid; (2) lævulic acid, and (3) a hexose which separates from water in crystals which contain H_2O , and melts at 93° , or from methyl alcohol in an anhydrous form melting at 148° (corr.); it exhibits birotation, the final value of $[\alpha]_D$ for the anhydrous sugar being $+52\cdot60^\circ$; it does not yield a phenylmethyllosazone with *as*-phenylmethylhydrazine, and is hence an aldose. Its phenyllosazone separates in annular aggregates of slender needles, which melts at $201\cdot9^\circ$ and is decomposed by water; a solution of 0·2282 gram in 25 c.c. of glacial acetic acid has a rotation, $\alpha_D - 1\cdot5^\circ$. On oxidation with nitric acid of sp. gr. 1·15, the sugar yields *d*-tartaric acid, whilst with bromine it gives a pentahydroxyhexoic acid, the calcium salt of which, $(C_6H_{11}O_7)_2Ca$, gives a value of $[\alpha]_D (+10\cdot99^\circ \text{ at } 20^\circ)$ slightly higher than that of calcium gluconate. Fehling's solution is reduced by the hexose to a slightly less extent than by dextrose. It is not decided whether this sugar is identical or stereoisomeric with dextrose.

The amount of copper obtained by the action of caramelan on Fehling's solution varies considerably with the time of heating, but

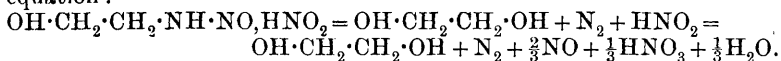
for 2 minutes' boiling is directly proportional to the amount of caramelan present in the solution.

When heated at 170—180°, sucrose only loses water, according to the equation: $C_{12}H_{22}O_{11} = C_{12}H_{18}O_9 + 2H_2O$; the caramelan thus obtained exhibits normal cryoscopic behaviour in aqueous solution. At a temperature of 190°, sucrose begins to lose carbon dioxide and small quantities of acetone.

T. H. P.

Aliphatic Amines. HANS EULER (*Arkiv. Kem. Min. Geol.*, 1903, 1, 67—76; *Annalen*, 1904, 330, 280—289).—In order to decide whether the vinylamine obtained by Gabriel from bromoethyl-phthalimide is really vinylamine or whether it must be regarded as ethyleneimine, the author has investigated its behaviour and that of methylamine towards nitrous acid. The results show that, although the reaction proceeds with different velocities in the two cases, its course is quite similar for both the bases. Further, it is found that the vinylamine (ethyleneimine) does not react with nitrous acid as do secondary amines, but behaves as follows: (1) 1 mol. of nitrous acid combines with the base forming a nitrite. (2) In the action of 1 mol. of nitrous acid on 1 mol. of the nitrite of the base, either the ring is unopened in the nitrite and then nitrous acid is added on and the ring broken: $\begin{array}{c} CH_2 \\ | \\ CH_2 \end{array} > NH_2 \cdot ONO \rightarrow OH \cdot CH_2 \cdot CH_2 \cdot NH_2(NO) \cdot O \cdot NO$, or

the nitrous acid reacts with the hydroxyethylamine nitrite already formed with evolution of water, in which case the analogy with the corresponding reaction of methylamine would be complete. Whichever of these two represents the actual course of the reaction, an unstable molecule is formed, and this decomposes according to the equation:



The results obtained with methylamine show that there is nothing special about the part played by the nitrous acid. The pure nitrite is extremely stable, but when an excess of free nitrous acid is present a much more vigorous evolution of gas occurs than with nitrous acid itself. These facts are explained by assuming that the nitrite and acid combine with loss of water and formation of $NO \cdot NH_2Me \cdot O \cdot NO$, which contains two nitrogen atoms in direct combination; since the basic character of the amine is annulled, or at any rate greatly diminished, by the entry of the NO group into the molecule, the HNO_2 originally in the molecule will be set free.

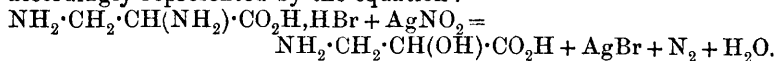
On the basis of the above representation, the reactions of ammonia and primary, secondary, and tertiary amines with nitrous acid may be explained from a common point of view. In all cases, a hydrogen atom of the nitrite is replaced by NO, by which means a compound is formed containing two nitrogen atoms in direct combination with one another. This nitroso-compound then immediately loses nitrous acid, and shows then a behaviour varying according to the possibilities of its decomposition: with ammonia or a primary amine, the molecule can split up into a hydroxyl compound (water or an alcohol) and nitrogen; in

the case of a secondary amine, the nitroso-compound contains no more hydrogen united to nitrogen and is stable, and with a tertiary amine, assuming the formation of a nitroso-compound, this must be immediately destroyed again, since only N_2O_3 , but not HNO_2 , can be given up.

T. H. P.

Conversion of Diaminopropionic Acid into *iso*Serine. ALEXANDER ELLINGER (*Ber.*, 1904, 37, 335—339. Compare Neuberg and Silbermann this vol., i, 220).—Since the discovery of serine (α -amino- β -hydroxypropionic acid) as a product of the hydrolysis of silk-fibroin (E. Fischer and Skita, *Abstr.*, 1902, i, 654) and of horn (E. Fischer and Dörpinghaus, *Abstr.*, 1903, i, 216), the importance of aminohydroxy-aliphatic acids has been emphasised.

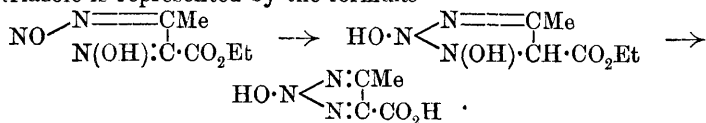
By the action of silver nitrite on an aqueous solution of $\alpha\beta$ -diaminopropionic monohydrobromide, no serine was obtained, but *isoserine* was isolated in a 20 per cent. yield and was identified by the formation of its copper and its phenylcarbimide derivatives (compare E. Fischer and Leuchs, *Abstr.*, 1903, i, 12). The essential action is accordingly represented by the equation:



When the mother liquor from the preparation of the *isoserine* was made alkaline and shaken with an ethereal solution of naphthalene- β -sulphonic chloride, naphthalene- β -sulphoserine was not obtained (compare E. Fischer and Bergell, *Abstr.*, 1903, i, 24).

A. McK.

Ethyl α -*iso*Nitroso- β -nitrosoaminobutyrate and its Derivatives. HANS EULER and ASTRID EULER (*Ber.*, 1904, 37, 47—49. Compare this vol., i, 146).—The compound $C_6H_9O_4N$, previously described, is shown to be identical with V. Meyer's ethyl *isonitroso*-acetoacetate, and the original product of the action of amyl nitrite on ethyl β -aminocrotonate is therefore ethyl α -*isonitroso*- β -nitrosoaminobutyrate, $ON \cdot N : CMe \cdot C(:NO \cdot NH_4) \cdot CO_2Et$. Its conversion into an isotriazole is represented by the formulæ



T. M. L

New Bases derived from Sugars. E. Roux (*Ann. Chim. Phys.*, 1904, [viii], 1, 72—144).—An account of work already published (compare *Abstr.*, 1901, i, 372; 1902, i, 266, 694; 1903, i, 73).

Acetylacetoneglucamine, $CH_2Ac \cdot CMe : N \cdot C_6H_{13}O_5$, crystallises in thin, felted needles, melts at 172° , is very soluble in water and less so in alcohol; 80 per cent. alcohol dissolves about 6 per cent. on boiling and only 1.6 per cent. at the ordinary temperature.

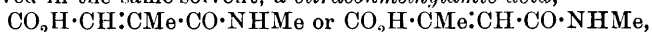
M. A. W.

Action of Ammonia on Itaconic Anhydride. JONE FOÀ (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1903, [iii], 9, 112—117).—The action of ammonia in alcoholic or benzene solution on itaconic anhydride

at the ordinary temperature or at 109° gives, after several hours, *itaconamide*, $\text{CO}_2\text{H}\cdot\text{C}_3\text{H}_4\cdot\text{CO}\cdot\text{NH}_2$, as sole product; it crystallises from alcohol in colourless needles and melts at $147\text{--}148^{\circ}$. At 180° , the *diamide*, $\text{CH}_2\text{:C}(\text{CO}\cdot\text{NH}_2)_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, is formed. It thus appears that the double linking in itaconic anhydride is different in its nature to that of maleic and citraconic anhydrides, which at once interact additively with ammonia forming amino-acids.

W. A. D.

Action of Methylamine on Citraconic Anhydride. SALVATORE GULLI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1903, [iii], 9, 164—167).—On adding a solution of methylamine in benzene to citraconic anhydride dissolved in the same solvent, a *citraconmethylamic acid*,



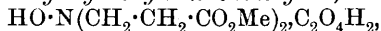
is obtained; it crystallises from absolute alcohol in white, deliquescent needles with a sweet taste, melts at $114\text{--}116^{\circ}$, and gives a *dibromide*, $\text{C}_6\text{H}_9\text{O}_3\text{NBr}_2$, also crystallising in small, deliquescent needles. From the benzene mother liquors of the acid, *methylamine citraconate*, $\text{CO}_2\text{H}\cdot\text{C}_3\text{H}_4\cdot\text{CO}\cdot\text{ONH}_3\text{Me}$, is obtained in silky needles melting at $120\text{--}122^{\circ}$.

Methylaminomethylaspartic acid is probably formed when molecular quantities of methylamine and citraconic anhydride are heated together in alcoholic solution at $105\text{--}110^{\circ}$, but cannot be isolated from the syrupy product.

W. A. D.

Action of Hydroxylamine on Unsaturated Esters. CARL D. HARRIES and WILHELM HAARMANN (*Ber.*, 1904, 37, 252—261. Compare Posner, this vol., i, 160).—*Methyl hydroxylaminodiacrylate-hydroxamic acid*, $\text{OH}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{N}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$, prepared by the interaction of methyl acrylate and hydroxylamine in presence of sodium, crystallises in nacreous, glistening needles melting at 124° , decomposes on keeping, gives a red coloration with ferric chloride, and reduces Fehling's solution in the cold.

The *oxalate* of *methyl hydroxylaminodiacrylate*,



is obtained by leaving the mother liquors from the above reaction in contact with anhydrous oxalic acid; it sinters at 125° and melts at $131\text{--}132^{\circ}$. The *hydrochloride* crystallises in plates, which sinter at 82° and melt at 92° .

[With ARTHUR STÄHLER.]—*Methylsantonate*, $\text{C}_{15}\text{H}_{21}\text{OMe}$, can be prepared either by direct esterification of santolic acid with methyl alcohol and sulphuric acid, or, better, by reducing methyl santonate with sodium amalgam. It crystallises in long, colourless needles melting at $111\text{--}114^{\circ}$, and forms an *acetate* which crystallises from alcohol in white plates melting at 151° .

E. F. A.

Compounds of Bismuth Salts with Thiocarbamide. KARL A. HOFMANN and K. L. GONDER (*Ber.*, 1904, 37, 242—245).—Bismuth nitrate and thiocarbamide react in cold alcoholic solution forming a compound, $\text{Bi}(\text{CSN}_2\text{H}_4)_3(\text{NO}_3)_2\cdot\text{OH}$, crystallising in citron-yellow plates; at 70° , red, prismatic needles belonging to the triclinic system are formed, having the formula $\text{Bi}(\text{CSN}_2\text{H}_4)_3(\text{NO}_3)_2\cdot\text{CSN}_2\text{H}_3$. Inter-

action in aqueous solution at 80° gives rise to a basic nitrate, $\text{Bi}(\text{CSN}_2\text{H}_4)_5(\text{NO}_3)_2 \cdot \text{OH}$. Bismuth chloride and thiocarbamide interact in alcoholic solution giving rise to a compound $\text{Bi}(\text{CSN}_2\text{H}_4)_2\text{Cl}_3$, crystallising in yellow rosettes, whereas in aqueous solution a red, crystalline substance, $\text{Bi}(\text{CSN}_2\text{H}_4)_3\text{Cl}_3$, is formed. As all these compounds are well characterised, it is hoped to use them for the separation of bismuth from polonium. E. F. A.

The Amphoteric Character of Cacodylic Acid. JAN VON ZAWIDZKI (*Ber.*, 1904, 37, 153—154).—The author's former paper (*Abstr.*, 1903, i, 801) contained an error in calculation. The dissociation constant for cacodylic acid as a base at 0° should be 1.15×10^{-14} , therefore ten times smaller than at 25° . The agreement of the values of K_{H} at 0° and 25° may be accidental, owing to the impurity of the water used, and both constants may have a considerable temperature-coefficient.

Both pseudo-acids and pseudo-bases are to be regarded as special cases of amphoteric electrolytes. C. H. D.

Preparation of Alkyl and Aryl Tin Compounds. PAUL PFEIFFER and K. SCHNURMANN (*Ber.*, 1904, 37, 319—322).—Tin tetraethyl, SnEt_4 , prepared by the action of magnesium ethyl bromide on tin tetrabromide, boils at 175° and is obtained free from triethylstannic bromide; the yield was 70 per cent. of the theoretical quantity, and 73 per cent. when stannic chloride was used. If only the theoretical quantity of ethyl bromide is used, triethylstannic bromide is produced, which, when extracted with ether and dried with potassium carbonate, is converted into a triethylstannic carbonate, $(\text{SnEt}_3)_2\text{CO}_3$, which, after distillation, separates in clear, transparent crystals and melts at 120° . The same method gave a yield of 81 per cent. of crude tin tetraphenyl and a yield of 57 per cent. of the pure product melting at 220° (Polis gives 225°).

Tribenzylstannic chloride, $\text{Sn}(\text{CH}_2\text{Ph})_3\text{Cl}$, forms glistening, white needles, melts at 127 — 130° , and decomposes when distilled.

T. M. L.

Fluorobenzene and some of its Derivatives. ARNOLD F. HOLLEMAN and J. W. BEEKMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 327—331. Compare *Abstr.*, 1902, i, 87).—Aniline sulphate was diazotised and the ice-cold solution poured with vigorous stirring into 55 per cent. hydrofluoric acid, heated nearly to the boiling point in a copper vessel. The fluorobenzene which distilled over was condensed by a freezing mixture.

p- and *m*-Fluoronitrobenzenes were prepared in an analogous manner from the corresponding nitroanilines. The three fluorotoluenes were also prepared from the toluidines. Anthranilic acid gave a small yield of *o*-fluorobenzoic acid, the main product being salicylic acid.

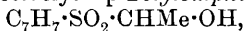
m-Fluoronitrobenzene melts at 1.7° , boils at 205° , and has the sp. gr. 1.2532 at 84.48° . *p*-Fluoronitrobenzene melts at 26.5° , boils at 205° , and has the sp. gr. 1.2583 at 84.48° . *p*-Fluoroaniline boils at

187°. 4-Fluoro-1-nitro-2-aminobenzene melts at 98°. Fluorobenzene melts at 41.2°, boils at 85°, and has the sp. gr. 1.0236 at 20°/4°.

Very little diphenyl was obtained by the action of sodium on an ethereal solution of fluorobenzene. Sodium does not abstract fluorine from an alcoholic solution of fluorobenzene. *m*- and *p*-Fluoronitrobenzenes, when heated with sodium methoxide, are quantitatively converted into the corresponding nitroanisoles. A. McK.

Oxidation of *o*-Nitrotoluene CHARLES LAUTH (*Bull. Soc. chim.*, 1904, [iii], 31, 133—134).—When *o*-nitrotoluene is oxidised with chromic acid mixture at 10—15°, only 6 to 8 per cent. of *o*-nitrobenzaldehyde is obtained. By suitably modifying the conditions, a yield of 80 per cent. of *o*-nitrobenzoic acid is procured, but no practical method of converting the acid into the aldehyde was found. With nitric acid, there was either no action or *o*-nitrobenzoic acid was produced, accompanied in some cases by nitrocresol. When potassium nitrate was added to a solution of *o*-nitrotoluene in sulphuric acid, there was formed, at 100°, 1:2:4-trinitrotoluene. When the substance was warmed with nitric acid in presence of reducing agents, small quantities of the aldehyde were obtained. "Nitrous fumes," prepared by the action of nitric acid on arsenious oxide, when passed into *o*-nitrotoluene at 150—200° gave *o*-nitrobenzaldehyde at first and the corresponding acid eventually. Nitrogen peroxide, prepared by heating lead nitrate, transformed *o*-nitrotoluene completely into *o*-nitrobenzoic acid. T. A. H.

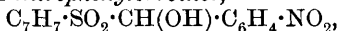
Additive Reactions of Sulphinic Acids. ELMER P. KOHLER and MARIE REIMER (*Amer. Chem. J.*, 1904, 31, 163—184).—Sulphinic acids readily unite with aliphatic aldehydes with formation of hydroxysulphones. These compounds are unstable; they gradually undergo decomposition in the air, and in solution are rapidly dissociated into their components. The following compounds were obtained by the action of toluene-*p*-sulphinic acid on acetaldehyde, isobutyraldehyde, and heptaldehyde respectively. *p*-Tolylsulphone-ethyl alcohol,



crystallises in thick plates, softens at 52°, and is completely melted at 72°. *p*-Tolylsulphoneisobutyl alcohol, $\text{C}_7\text{H}_7\cdot\text{SO}_2\cdot\text{CH}(\text{OH})\cdot\text{CHMe}_2$, crystallises from ether in colourless needles. *p*-Tolylsulphoneheptyl alcohol, $\text{C}_7\text{H}_7\cdot\text{SO}_2\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_{13}$, crystallises in white, slender needles and is decomposed on heating.

Toluene-*p*-sulphinic acid yields a similar series of compounds with aromatic aldehydes, but these substances are much more stable than those obtained with the aliphatic aldehydes. The two following compounds were obtained with *m*- and *p*-nitrobenzaldehyde respectively.

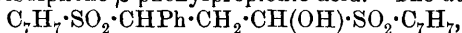
p-Tolylsulphone-*m*-nitrophenylcarbinol,



crystallises in white, slender needles and melts at 110°. *p*-Tolylsulphone-*p*-nitrophenylcarbinol crystallises in pale yellow needles and melts at 116°; it is decomposed by aniline, and it dissolves in acetic anhydride with formation of the acetal of *p*-nitrobenzaldehyde.

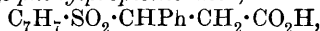
Toluene-*p*-sulphinic acid combines with cinnamaldehyde with

formation of a monosulphone and a disulphone. The *monosulphone*, $C_7H_7 \cdot SO_2 \cdot CHPh \cdot CH_2 \cdot CHO$, forms white, globular masses of crystals and melts at 78° ; it unites with potassium hydrogen sulphite to form a crystalline compound, and when oxidised with dilute nitric acid it yields β -*p*-tolylsulphone- β -phenylpropionic acid. The *disulphone*,



crystallises in white needles and melts and decomposes at about 126° .

β -p-Tolylsulphone- β -phenylpropionic acid,



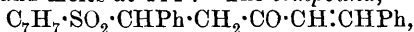
prepared by the action of toluene-*p*-sulphinic acid on cinnamic acid, crystallises from hot water in slender needles, melts at 197 — 198° , and is readily soluble in alcohol or ether; its *methyl* ester melts at 156° ; its *sodium*, *calcium*, and *barium* salts are described.

β -Phenylsulphone- β -phenylpropionic acid, $SO_2Ph \cdot CHPh \cdot CH_2 \cdot CO_2H$, obtained by the action of benzenesulphinic acid on cinnamic acid, crystallises from hot water in lustrous plates, melts at 173° , and is readily soluble in alcohol or ether; its *ethyl* ester melts at 139° ; the *barium* salt is described.

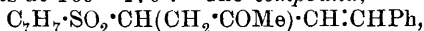
β -p-Tolylsulphonepropionic acid, $C_7H_7 \cdot SO_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$, is formed by the action of toluene-*p*-sulphinic acid on fumaric or maleic acid, but is best obtained in a pure state by treating β -iodopropionic acid with sodium *p*-toluenesulphinate; it crystallises in needles and melts at 110 — 113° .

p-Tolylsulphonepyrotartaric acid, $C_7H_7 \cdot SO_2 \cdot CMe(CO_2H) \cdot CH_2 \cdot CO_2H$, obtained by the action of toluene-*p*-sulphinic acid on citraconic acid, crystallises in small, lustrous prisms, melts at 169 — 171° , and is extremely soluble in alcohol, ether, or acetone; its *sodium* salt is described.

Toluene-*p*-sulphinic acid readily unites with unsaturated ketones. The following compounds were obtained by its combination with benzylideneacetone, dibenzylideneacetone, benzylideneacetophenone, cinnamylideneacetone, and cinnamylideneacetophenone respectively. The *compound*, $C_7H_7 \cdot SO_2 \cdot CHPh \cdot CH_2 \cdot COMe$, crystallises from alcohol in white, slender needles and is decomposed by bleaching powder with formation of chloroform and β -*p*-tolylsulphone- β -phenylpropionic acid; when treated with phenylhydrazine, it yields the phenylhydrazone of benzylideneacetone, phenylhydrazine toluene-*p*-sulphinate, and 1 : 5-*di-phenyl-3-methylpyrazoline*, $NPh \langle \begin{smallmatrix} CHPh \\ N : CMe \end{smallmatrix} \rangle CH_2$, which forms long, pale yellow crystals and melts at 114° . The *compound*,

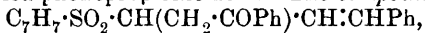


crystallises in long, slender needles and melts at 189° ; on oxidation with potassium permanganate, it is converted into benzaldehyde, benzoic acid, and β -*p*-tolylsulphone- β -phenylpropionic acid. It unites with 2 atoms of bromine to form a *dibromo*-compound which crystallises in needles. The *compound*, $C_{22}H_{20}O_3S$, formed by the action of toluene-*p*-sulphinic acid on benzylideneacetophenone, crystallises in needles and melts at 169 — 170° . The *compound*,



crystallises from alcohol and melts at 125 — 126° ; when warmed with a concentrated solution of bleaching powder, it yields benzoic acid and

other products, which, on oxidation with potassium permanganate, furnish β -*p*-tolylsulphonepropionic acid. The compound,

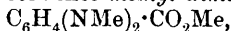


crystallises from acetone in needles and melts at 145° .

E. G.

Aromatic Betaines. II. RICHARD WILLSTÄTTER and WALTER KAHN (*Ber.*, 1904, 37, 401—417. Compare *Abstr.*, 1902, i, 266).—Unlike the fatty α -betaines, the transformation of aromatic betaines by heat is not affected by the relative position of the carbonyl and the basic group.

In the methylation of anthranilic acid by means of methyl iodide and sodium hydroxide, not more than two methyl groups can be introduced, the compound described by Lauth (*Abstr.*, 1894, i, 86) as the hydriodide of *o*-benzobetaine being, in fact, the salt of dimethylantranilic acid, and Lauth's dimethylantranilic acid being methylantranilic acid. The betaine is best prepared by methylation of methyl methylantranilate, which is readily obtained from anthranilic acid and methyl sulphate (F. Ullmann, *Abstr.*, 1903, i, 394). Methyl iodide converts it in the cold into methyl dimethylantranilate,



an uncrystallisable oil boiling at 160 — 161° under 38 mm. or at 130 — 131° under 11.5 mm. pressure. The hydriodide forms sparingly soluble needles and leaflets and melts at 163° . Prolonged boiling with water hydrolyses the ester, forming dimethylantranilic acid, crystallising from ether in long, white needles and melting at 70° , dissolving readily in water or alcohol, sparingly in cold ether. The aurichloride, $(\text{C}_9\text{H}_{11}\text{O}_2\text{N})_2\cdot\text{HAuCl}_4$, crystallises from boiling alcohol in large, yellow prisms and decomposes above 100° . Methyl dimethylantranilate methiodide crystallises from water in colourless prisms and melts at 153° .

Methyl *m*-dimethylaminobenzoate methiodide forms small needles, which dissolve sparingly in alcohol or cold water and melt and decompose at 220 — 221° . The corresponding para-compound crystallises from alcohol in silvery, glistening, six-sided tablets and melts and decomposes at 170° .

o-Benzobetaine, $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix} \text{NMe}_3 \\ \text{CO} \end{smallmatrix}\right\rangle\text{O}$, prepared by the action of moist

silver oxide on the iodide, crystallises from absolute alcohol in highly refractive tablets and hollow pyramids, containing $\frac{1}{2}\text{H}_2\text{O}$, and melts at 224° . After removal of the water, which is only complete after heating at 120° for 2 weeks under reduced pressure, it melts at 227° . It dissolves readily in water, sparingly in cold alcohol or acetone, and is insoluble in ether. The platinichloride forms large tablets, the picrate forms slender needles. The aurichloride forms slender, yellow needles, darkens on heating, and melts and decomposes at 206° ; the hydriodide forms thick, square prisms containing H_2O , and melts at 138° . Anhydrous *o*-benzobetaine is converted by heating at 240 — 245° into methyl dimethylantranilate, a small quantity of dimethylaniline being always formed at the same time, and predominating when moisture is present. The latter base is removed in the form of phenyltrimethylammonium iodide by the addition of methyl iodide.

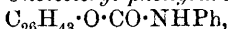
p-Benzobetaine (compare Michael and Wing, Abstr., 1886, 148) is readily prepared from *p*-aminobenzoic acid. Heating at 110° converts it quantitatively into methyl *p*-dimethylaminobenzoate.

Phenyldimethylbetaine (phenyldimethylglycine) is best prepared by the method of Reitzenstein (Abstr., 1903, i, 435), and crystallises from alcohol in aggregates of small, transparent crystals containing H₂O, and melts at 123—124°. The water is not completely removed by heating. The *picrate* forms slender needles, and decomposes at 195°. Heating the betaine at 170—175° converts it into phenyldimethylglycine, forming a *methiodide* melting at 98—99°. A small quantity of dimethylaniline is also produced. C. H. D.

Action of Nitrous Acid on Phenylcarbamide. R. DONT and J. HAAGER (*Monatsh.*, 1903, 24, 844—856).—Phenylcarbamide reacts readily with nitrous acid with little evolution of gas. When only 1½ mols. of hydrogen chloride are present, nitrosophenylcarbamide, NO·NPh·CO·NH₂, is formed. In presence of an excess of hydrochloric acid, this is decomposed into diazobenzene chloride and carbamic acid, which then breaks up into water and isocyanic acid. The diazobenzene chloride and isocyanic acid then combine to form phenylcarbimide, nitrogen being set free. Alcoholic potassium hydroxide or potassium ethoxide reacts with nitrosophenylcarbamide, forming potassium isocyanate and potassium phenylnitrosoamine. Thus, when nitrous acid reacts with phenylcarbamide, suspended in an excess of hydrochloric acid, oily drops of phenylcarbimide separate, and diazobenzene chloride is found in the solution. C. H. D.

Action of Phenylcarbimide on Certain Monohydric Alcohols.

II. ARMAND BLOCH (*Bull. Soc. chim.*, 1904, [iii], 31, 71—76. Compare this vol., ii, 152).—*Cholesteryl phenylurethane*,



obtained by heating cholesterol with phenylcarbimide at 180°, melts at 168—169°, is readily soluble in ether, chloroform, or benzene in the cold, and in alcohol or light petroleum when heated. It has $[\alpha]_D - 28.19^\circ$ at 19° in benzene when $c = 2.07$ per cent., gives an orange-yellow coloration with sulphuric acid, and the usual cholesterol reactions with Hesse's and Salkowski's reagents. It decomposes at 68—70° when heated in test-tubes, and at 280° when heated in open vessels, evolving carbon dioxide and leaving a brown, fluorescent liquid from which aniline, diphenylcarbamide, and a crystalline *substance* melting at 138—140° were isolated.

When heated in a closed tube at 350°, cholesteryl phenylurethane decomposes into aniline, cholesterol, and a *cholesterilene*, C₂₆H₄₂, which crystallises in needles, melts at 75.5°, has $[\alpha]_D - 97.85$ —98° in benzene when $c = 2.08$ per cent., and -100.25° when $c = 1.04$ per cent., gives a citron-yellow coloration with sulphuric acid, and the usual cholesterol colour reactions.

This cholesterilene is similar to, but probably not identical with, that described by Mauthner and Suida (Abstr., 1896, i, 425), which, the author finds, melts at 74° and has $[\alpha]_D - 71.88^\circ$ at 18° in benzene when $c = 0.626$ per cent.

Cholesteryl phenylurethane, when heated with ammonia in closed tubes, furnishes ammonium carbonate, aniline, and cholesterol; the latter has $[\alpha]_D - 40.46^\circ$ at 19° in chloroform when $c = 1.85$ per cent., whereas commercial cholesterol, twice recrystallised from alcohol, has $[\alpha]_D - 40.37^\circ$ at 19° in chloroform when $c = 1.80$ per cent.

When heated with aniline, either in closed tubes or under atmospheric pressure, cholesteryl phenylurethane decomposes partially into diphenylcarbamide and cholesterol; it is scarcely attacked by barium hydroxide or a 10 per cent. solution of potassium hydroxide, but a 50 per cent. solution of the latter decomposes it, forming carbon dioxide, aniline, and cholesterol. It is pointed out that phenylurethanes are only readily obtained from the monohydric alcohols containing less than thirty carbon atoms in the molecule, and that they are all crystalline with the exception of octyl phenylurethane.

Hexadecyl and cholesteryl phenylurethanes are exceptionally stable towards heat. T. A. H.

Condensation of Oximes with Thiocarbimides. BRONISLAW PAWLEWSKI (*Ber.*, 1904, 37, 158—160).—The thiocarbimides readily condense with oximes to form derivatives of thiocarbamide. Phenylthiocarbimide combines with α - or β -benzaloxime, dissolved in toluene, forming diphenylthiocarbamide, $\text{CS}(\text{NHPh})_2$. *o*-Tolylthiocarbimide and benzaloxime form *phenyl-o-tolylthiocarbamide*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$, crystallising from alcohol in slender, glistening needles melting at 166 — 168° . This does not appear to be identical with the compound obtained by Staats (*Abstr.*, 1880, 386) from aniline and *o*-tolylthiocarbimide. *Phenyl-p-tolylthiocarbamide* crystallises in thick needles melting at 176 — 178° and is probably isomeric with the compound obtained by Staats, Gebhardt (*Abstr.*, 1884, 1320) and Marckwald (*Abstr.*, 1892, 1326). Camphoroxime combines slowly with phenylthiocarbimide, dissolved in benzene, and after several months *phenylcamphanylthiocarbamide*, $\text{C}_{10}\text{H}_{17}\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$, separates, crystallising from alcohol in needles and leaflets melting at 150 — 152° . The reaction occurs rapidly on heating. A probably isomeric compound has been obtained by Goldschmidt and Schulhof (*Abstr.*, 1886, 557).

C. H. D.

Methyl and Ethyl Ethers of *p*-Hydroxyphenylhydroxylamine and the Derived Azoxy-compounds. ADOLF RISING (*Ber.*, 1904, 37, 43—47).—*p*-Anisylhydroxylamine, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{OH}$, forms glistening, white scales or flat needles, melts at about 98° , but sometimes resolidifies at this temperature, and liberates gas when again fused to a clear liquid. *p*-Nitrosoanisole, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NO}$, crystallises from light petroleum and melts at 23° ; the product melting at 32 — 34° , described by Baeyer and Knorr as an oxidation product from *p*-anisidine and Caro's acid, contained considerable quantities of *p*-nitroanisole. A theoretical yield of *p*-azoxyanisole was obtained by the interaction of the two preceding compounds, and the substance showed the turbidity ('liquid crystals') first described by Gattermann.

p-Phenetylhydroxylamine, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{OH}$, forms white, glistening scales and melts at 91.5 — 92° when heated from 75° , but the melting

point is dependent on the rate of heating; the substance begins to decompose in the course of a few hours, but can be purified by recrystallising from ether. *p*-Nitrosophenetole crystallises from light petroleum in large, bluish-green prisms and melts at 33—34°. The *p*-azoxyphenetole prepared from these two compounds melted at 137·4—137·9° and became clear at 168—168·5°, that is, 3° above the temperatures given by Gattermann. *p*-Anisoleazoxy-*p*-phenetole, however, prepared from *p*-phenetylhydroxylamine and *p*-nitrosoanisole, melted at 93·5—94° and became clear at 149·6°, temperatures considerably higher than those recorded by Gattermann and Ritschke (Abstr., 1890, 1119). T. M. L.

Behaviour of Aminophenols towards Caro's Reagent. EUGEN BAMBERGER and MAX CZERKIS (*J. pr. Chem.*, 1903, [ii], 68, 473—480. Compare Abstr., 1903, i, 624).—Caro's reagent oxidises *o*-aminophenol to *o*-nitrophenol, together with an unknown nitroso-compound and a compound which crystallises in red needles and melts at 156·5°, and yields *o*-aminophenol on reduction. *m*-Aminophenol yields *m*-nitrophenol, 3- and 4-nitrocatechol, and *m*-azoxyphenol, $\text{ON}_2(\text{C}_6\text{H}_4\cdot\text{OH})_2$ (Nölting and Federmann, *Chem. Zeit.*, 1902, 26, 52). The latter compound was also prepared from *m*-nitrophenetole by reduction to *m*-ethoxyphenylhydroxylamine, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{OH}$, white, silky needles melting at 61—61·5°, and oxidation, followed by hydrolysis of the ethoxy-groups. The oxidation product from *m*-aminophenol also contains acetaldehyde, the formation of which is unexplained.

p-Aminophenol is oxidised in ethereal solution to *p*-nitrosophenol and *p*-nitrophenol; in aqueous solution, quinone and quinol are formed.

C. H. D.

Oxidation of *m*- and *p*-Nitrophenols with Caro's Reagent. EUGEN BAMBERGER and MAX CZERKIS (*J. pr. Chem.*, 1903, [ii], 68, 480—485).—Caro's reagent oxidises a solution of *m*-nitrophenol in water on warming, with formation of 3- and 4-nitrocatechols, a hydroxyl group being thus directly introduced. A part of the nitrophenol is broken down, carbon dioxide being evolved, and an oily compound, showing the reactions of an organic peroxide, is formed. On distilling the oil, or on warming its aqueous solution, succinic acid is formed.

p-Nitrophenol is best oxidised by Caro's reagent in the pasty form. 4-Nitrocatechol and the oily peroxide are obtained. *o*-Nitrophenol resists oxidation; 3-nitrocatechol was isolated from the product.

C. H. D.

Oxidation of Phenol with Caro's Reagent. EUGEN BAMBERGER and MAX CZERKIS (*J. pr. Chem.*, 1903, [ii], 68, 486).—Caro's reagent oxidises phenol at the ordinary temperature, forming catechol, quinhydrone, and small quantities of other compounds, not yet investigated.

C. H. D.

Pyrogallol. ALFRED EINHORN, J. COBLINER, and H. PFEIFFER (*Ber.*, 1904, 37, 100—123).—It has been shown (Einhorn, Abstr., 1898, i, 409) that monohydric phenols form only carbonates of the

formula $\text{CO}(\text{OR})_2$, whilst *o*-dihydric phenols form internal carbonates, $\text{R}''\text{C}_6\text{H}_3\text{C}_6\text{H}_3\text{CO}$, and *m*- and *p*-dihydric phenols form polymolecular carbonates. Pyrogallol is found to form only two carbonates, the reactions of which have now been studied.

On passing a current of phosgene gas into a solution of pyrogallol in a mixture of pyridine and xylene and boiling, an oil separates, becoming syrupy on cooling. The xylene is separated, and the oil decomposed by cooled dilute hydrochloric acid, which precipitates *pyrogallol carbonate*, $\text{OH}\cdot\text{C}_6\text{H}_3\text{C}_6\text{H}_3\text{CO}$, crystallising from benzene in colourless needles or tablets melting at $132\text{--}133^\circ$. The same product is obtained by heating pyrogallol with phenol carbonate. It has a sweet taste and dissolves sparingly in water, the solution gradually decomposing, readily soluble in ether, acetone, ethyl acetate, or acetic acid. Ferric chloride gives a violet-brown coloration, destroyed by hydrochloric acid. The molecular weight in benzene solution is normal.

Dipyrogallol tricarbate, $\text{CO}(\text{O}\cdot\text{C}_6\text{H}_3\text{C}_6\text{H}_3\text{CO})_2$, prepared by the same method, but employing a larger quantity of phosgene, crystallises in colourless leaflets melting at 177° , and dissolves sparingly in alcohol, ether, or benzene. It is only slowly attacked by boiling water, and even warm sodium carbonate only causes decomposition after a long time.

Benzoylpyrogallol carbonate, $\text{OBz}\cdot\text{C}_6\text{H}_3\text{C}_6\text{H}_3\text{CO}$, crystallises from benzene in white, nodular masses and melts at 149° . Ferric chloride produces no coloration.

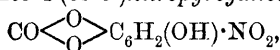
Pyrogallol carbonate is converted by boiling with methyl alcohol into *pyrogallol methyl carbonate*, $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{O}\cdot\text{CO}_2\text{Me}$, crystallising from a mixture of benzene and chloroform and melting at 120° . This and the similar derivatives obtained by the action of alcohols or bases on the carbonate give the green catechol coloration with ferric chloride, indicating that the two remaining hydroxyl groups are in the ortho-position. *Pyrogallol ethyl carbonate* crystallises from a mixture of chloroform and light petroleum in small, white needles and melts at 74° . *Pyrogallol diethylcarbamate*, $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{O}\cdot\text{CO}\cdot\text{N}(\text{Et})_2$, from pyrogallol carbonate and diethylamine, crystallises from alcohol in rhombic tablets and melts at 149° . Piperidine forms *pyrogallol piperidine-1-carboxylate*, $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{O}\cdot\text{CO}\cdot\text{C}_5\text{H}_{10}\text{N}$, which crystallises from ethyl acetate in colourless needles and melts at 161° . *Pyrogallol phenylcarbamate*, $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{O}\cdot\text{CO}\cdot\text{NHPh}$, crystallises from benzene in long needles and melts at 141° . *Pyrogallol p-phenethylcarbamate*, $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{O}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$, separates from a mixture of benzene and ethyl acetate in needles melting at 162° .

Pyrogallol carbonate combines with quinoline to form a compound, $\text{CO}\text{C}_6\text{H}_3\text{C}_6\text{H}_3\text{C}_6\text{H}_3\text{N}$, separating from a mixture of benzene and light petroleum in colourless needles and melting at 103° . Triethylamine forms the compound, $[\text{CO}\text{C}_6\text{H}_3(\text{OH})]_2\cdot\text{N}(\text{Et})_3$, which may be

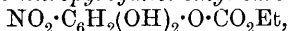
an oxonium compound, or may contain the second molecule of carbonate as phenol of crystallisation. It forms colourless needles, melting at 111° and decomposing on exposure to air.

Bromopyrogallol carbonate, $\text{CO} \begin{smallmatrix} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{smallmatrix} \text{C}_6\text{H}_2\text{Br}\cdot\text{OH}$, prepared by the action of bromine on a cooled solution of the carbonate in dry chloroform, crystallises from benzene in colourless crystals melting at 155° , dissolving readily in ether, sparingly in benzene or chloroform. The bromine atom probably occupies either the 4- or 6-position. Carbon dioxide is evolved on boiling with water, forming *bromopyrogallol*, which crystallises from benzene in thick prisms, blackens at 120° , and decomposes at about 140° . By further bromination in presence of iron, *dibromopyrogallol carbonate* is obtained in needles melting at 146° , and decomposing into *dibromopyrogallol*, which forms long needles melting at 158° , on boiling with water.

A cooled mixture of concentrated nitric and sulphuric acids converts pyrogallol carbonate into 4-(or 6-)*nitropyrogallol carbonate*,



which crystallises from chloroform in long, slightly yellow needles melting at 148 – 149° , and dissolves readily in ether, acetone, or ethyl acetate, sparingly in water, acetic acid, or benzene. Boiling alcohol converts it into *nitropyrogallol ethyl carbonate*,



crystallising from dilute alcohol in yellow leaflets, melting at 134° , and dissolving in alkalis to yellow solutions. Bromine converts it into *bromonitropyrogallol ethyl carbonate*, which forms bright yellow needles melting at 172° . Boiling water decomposes nitropyrogallol carbonate, forming 4-*nitropyrogallol*, which crystallises from water or benzene in groups of needles melting at 162° , and dissolving readily in alcohol, ether, acetic acid, or ethyl acetate. The *dipotassium* and *diammonium* salts are reddish-brown, and cannot be recrystallised, the *quinoline* salt forms unstable, fluorescent, yellow needles and melts at 74° . Bromine forms *bromonitropyrogallol*, crystallising from benzene in yellow masses and melting at 122° , dissolving readily in ether, sparingly in water or chloroform. *Benzoyl-4-nitropyrogallol* crystallises from benzene in slender, yellow needles melting and decomposing at 214° .

Triacetyl-4-nitropyrogallol, $\text{NO}_2\cdot\text{C}_6\text{H}_2(\text{OAc})_3$, forms yellow needles melting at 85° , and dissolves readily in ether, sparingly in benzene or alcohol. Nitropyrogallol may be methylated with methyl sulphate; the *trimethyl ether* separates from dilute alcohol in colourless crystals and melts at 44° . Tin and hydrochloric acid reduce nitropyrogallol to 4-*aminopyrogallol hydrochloride*, which forms colourless needles and dissolves in water and alcohol to solutions which darken when kept. Benzoyl chloride reacts with it at 150° to form 5:6-*dibenzoyloxy-1-phenylbenzoxazole*, $\text{C}_6\text{H}_2(\text{OBz})_2 \begin{smallmatrix} \diagup \text{O} \diagdown \\ \diagdown \text{N} \diagup \end{smallmatrix} \text{CPh}$, which crystallises from benzene-light petroleum in white needles and melts at 144° .

When a solution of aminopyrogallol hydrochloride is boiled for 8 hours, a current of carbon dioxide being passed through it, 1:2:3:4-*tetrahydroxybenzene* is obtained, crystallising from benzene

in colourless needles melting at 161° and dissolving readily in water ether, alcohol, or ethyl acetate. Methyl sulphate forms an ether melting at 83° , which seems to be identical with Ciamician and Silber's tetramethylapionol, melting at 89° (Abstr., 1896, i, 608). The *tetra-acetyl*-derivative crystallises from a mixture of alcohol and light petroleum in needles melting at 136° ; the *tetrabenzoyl* derivative forms colourless leaflets.

Fuming nitric and sulphuric acids convert pyrogallol carbonate into 4:6-dinitropyrogallol, $C_6H(NO_2)_2(OH)_3$, which crystallises from hot water in long, yellow needles, melting at 208° , dissolving in alkalis to dark brown solutions. The *triacetyl* derivative forms colourless leaflets and melts at 154° . Reduction of the dinitro-compound with tin and hydrochloric acid gives 4:6-diaminopyrogallol hydrochloride, which reacts with benzoyl chloride to form 6-benzoyloxy-1:5-diphenylbenzodioxazole, $OBz \cdot C_6H \left[\begin{smallmatrix} \text{N} \\ \text{O} \end{smallmatrix} \right] CPh_2$, crystallising from benzene in colourless, felted needles and melting at 291° . Water converts the diaminohydrochloride into pentahydroxybenzene, $C_6H(OH)_5$, crystallising from benzene in microscopic needles, dissolving readily in alcohol, ether, or ethyl acetate, sparingly in water, insoluble in benzene (compare Wenzel and Weidel, this vol., i, 48). The *penta-acetyl* derivative forms colourless needles melting and decomposing at 165° .
C. H. D.

a-Phenyl-*a*-anisylpropene. CARL HELL and H. STOCKMAYER (Ber., 1904, 37, 225—230).—When phenyl anisyl ketone was submitted to the Grignard reaction with magnesium ethyl iodide, *a*-phenyl-*a*-anisylethylcarbinol was not isolated as a product of the action, but *a*-phenyl-*a*-anisylpropene, $OMe \cdot C_6H_4 \cdot CPh : CHMe$, presumably formed from the carbinol by abstraction of water, was obtained instead; it separates from methyl alcohol in glistening leaflets, melts at 54° , and distils unchanged at about 312° under the ordinary pressure. When bromine is added to its chloroform solution, hydrogen bromide is evolved and *β* -bromo-*a*-phenyl-*a*-anisylpropene, $OMe \cdot C_6H_4 \cdot CPh : CBrMe$, is formed; this separates from ether in tiny needles and melts at 51 — 52° ; when bromine is added to its chloroform solution, hydrogen bromide is evolved, and a crystalline substance, $C_{16}H_{24}OBr_2$, melting at 98 — 99° , were isolated, the product probably being a substitution product containing bromine in the anisyl group. Bromophenylanisylpropene is not attacked by sodium ethoxide.
A. McK.

Aromatic Propene Derivatives. III. CARL HELL and H. BAUER (Ber., 1904, 37, 230—233. Compare preceding abstract).—*aa*-Diphenylpropene, $CPh_2 : CHMe$, and *a*-phenyl-*a*-methylpropene, $CMePh : CHMe$, behave like phenylanisylpropene with respect to the action of bromine.

Diphenylethylcarbinol, $CEtPh_2 \cdot OH$, prepared by the application of Grignard's reaction to benzophenone with magnesium ethyl iodide, melts at 94 — 95° . When boiled with acetic anhydride, it forms *aa*-diphenylpropene, which crystallises from alcohol in leaflets and melts at 52° . *β* -Bromo-*aa*-diphenylpropene, $CPh_2 : CBrMe$, prepared by the action of bromine on a chloroform solution of diphenylpropene,

separates from alcohol in needles, melts at 48—49°, and boils at 169—170° under 12 mm. pressure. It is not attacked by sodium ethoxide. *β-Bromo-α-phenyl-α-methylpropene*, $\text{CMePh}:\text{CBrMe}$, prepared by the action of bromine on phenylmethylpropene (compare Klages, *Abstr.*, 1902, i, 666; 1903, i, 19), is a yellow oil which boils at 114—116° under 13 mm. pressure. It is not attacked by sodium ethoxide. A. McK.

Preparation of Stilbene, 4-Methoxystilbene, and α-Methylstilbene. CARL HELL (*Ber.*, 1904, 37, 453—458).—Benzaldehyde is added to an ethereal solution of magnesium benzyl chloride, the mixture decomposed with water and dilute sulphuric acid, and the residue from the ethereal solution distilled. The yield of stilbene is good. If the product is not distilled, phenylbenzylcarbinol, $\text{CH}_2\text{Ph}\cdot\text{CHPh}\cdot\text{OH}$, is obtained as glistening needles melting at 66—67° (compare Limpricht and Schwanert, *Annalen*, 155, 62; Goldenberg, *ibid.*, 174, 332; Knoevenagel and Arndts, *Abstr.*, 1902, i, 548; Sudborough, *Trans.*, 1893, 67, 605).

Anisaldehyde and magnesium benzyl chloride yield, without distillation of the product, *p*-methoxystilbene (compare von Walther and Wetzlich, *Abstr.*, 1900, i, 438).

Phenylbenzylmethylcarbinol, $\text{CH}_2\text{Ph}\cdot\text{CMePh}\cdot\text{OH}$, obtained from acetophenone and magnesium benzylchloride, melts at 50—51° and distills under atmospheric pressure, or at 175° under 15 mm. pressure, without being decomposed. On treatment with acetic anhydride, it yields α-methylstilbene (compare *Abstr.*, 1902, i, 668). J. J. S.

Reaction between Benzene and Formaldehyde. ALEXANDER M. NASTUKOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 824—831).—The interaction of benzene and formaldehyde in presence of concentrated sulphuric acid yields a compound to which the author gives the name *phenylformol*. It is insoluble in all solvents and differs from the compound formed from benzene and cellulose (see *Abstr.*, 1902, i, 362 and 747) in being very stable towards the action of reagents; thus, excess of chromic acid in acetic acid solution, phosphorus pentachloride, and hydrobromic acid in a sealed tube are all without action on it. Its composition is: carbon, 87.29; hydrogen, 6.78; oxygen, 5.23; and sulphur, 0.70 per cent. On dry distillation, it yields about 50 per cent. of its weight of an oil containing 12 per cent. (on the weight of oil) of diphenylmethane, 7 of toluene, 3 of phenyl-*p*-tolylmethane, 2 of *p*-xylene, 2 of anthracene and synanthrene, and 1 of benzene. Working under definite conditions, this method may be employed for the preparation of diphenylmethane from formalin.

The formation of diphenylmethane shows that the phenyl groups replace the oxygen or the hydroxyl, whilst in the case of the cellulose compound (*loc. cit.*) they replace the hydrogen. T. H. P.

Constitution of Phenylcinnamenylacrylic Acid Dibromide. ARTHUR MICHAEL and VIRGIL L. LEIGHTON (*J. pr. Chem.*, 1903, [ii], 68, 521—534).—The dibromide of phenylcinnamenylacrylic acid is assumed by Thiele and Rössner (*Abstr.*, 1899, i, 612) to contain the bromine

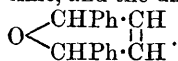
atoms in the $\alpha\delta$ -positions, on account of its conversion by alkali into diphenylhydrofuran. The conversion into a γ -lactone by heating with diethylaniline, however, suggests the $\gamma\delta$ -positions for the bromine atoms, and is explained by Thiele as being due to the formation and dissociation of diethylaniline hydrobromide. The formation of lactone takes place, however, at 150° , at which temperature the diethylaniline salt is not dissociated. The reactions are now shown to be explicable on the assumption of the $\gamma\delta$ -constitution.

The addition of bromine to phenylcinnamenylacrylic acid is best carried out at 0° in carbon disulphide solution in direct sunlight. After recrystallisation from alcohol, the dibromide melts at 180 — 181° . An amorphous isomeride is also obtained, yielding a *methyl* ester, which crystallises from methyl alcohol in six-sided prisms and melts at 133 — 134° . A portion of the ester remains uncrystallisable and appears to contain a third isomeride.

Methyl phenylcinnamenylacrylate, crystallising from methyl alcohol in thick prisms and melting at 82 — 83° , combines with bromine to form a dibromide identical with that obtained by Thiele by esterifying the dibromide of the acid, and melting at 118° . An amorphous dibromide was also obtained.

Oxidation of the acid dibromide gives a means of distinguishing between the $\alpha\delta$ - and $\gamma\delta$ -constitutions: $\text{CO}_2\text{H}\cdot\text{CPhBr}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHBrPh}$ giving $\text{CPhBr}\cdot(\text{CO}_2\text{H})_2$, and $\text{CO}_2\text{H}\cdot\text{CHPh}\cdot\text{CH}\cdot\text{CHBr}\cdot\text{CHBrPh}$ giving $\text{CHPhBr}\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$ and $\text{COPh}\cdot\text{CO}_2\text{H}$. The oxidation is carried out by means of potassium permanganate in acetone solution (F. Sachs, Abstr., 1901, i, 272), and is imperfect, but benzoylformic acid was recognised among the products. Better results are obtained from the methyl ester melting at 118° , which yields the dibromide of cinnamic acid and benzoylformic acid on careful oxidation with potassium permanganate in acetone solution. Benzoic acid is also formed by the decomposition of cinnamic acid dibromide into hydrogen bromide and α -bromocinnamic acid, the latter being then oxidised to benzoic acid. The isomeric methyl ester dibromide melting at 134° yielded methyl benzoylformate on oxidation.

A solution of potassium hydroxide (1—2 mols.) converts the acid dibromide, at the ordinary temperature, into diphenyldihydrofuran. In this case, the γ -bromine atom is probably replaced by hydroxyl, potassium bromide and carbon dioxide being removed at the same time, and the unsaturated carbinol then passes into the furan derivative,



When a larger quantity of potassium hydroxide is employed, hydrogen bromide is rapidly removed with the formation of phenylbromocinnamenylacrylic acid. Potassium hydroxide converts the methyl ester dibromide, melting at 134° , into *methyl phenylbromocinnamenylacrylate*, crystallising from methyl alcohol and melting at 81 — 82° , isomeric with the ester prepared by Thiele melting at 128° .

When the liquid acid dibromide reacts with a small quantity of potassium hydroxide, diphenyldihydrofuran is formed; excess of alkali forms *phenylcinnamenylacrylic acid*, melting at 200 — 201° , and isomeric with Thiele and Rössner's acid, together with a crystalline acid which was not obtained in a pure state.

C. H. D.

Nitrophthalaldehydic Acids. RUDOLF WEGSCHEIDER and LEO KUŠY VON DÚBRAV (*Monatsh.*, 1903, 24, 805—831).—Phthalaldehydic acid (*o*-aldehydobenzoic acid) is not nitrated by boiling with glacial acetic acid and fuming nitric acid, anhydrides being formed. A better result is obtained when a solution of phthalaldehydic acid in cold concentrated sulphuric acid is nitrated with potassium nitrate and the product poured into water. A white precipitate separates, consisting of a mixture of the anhydrides of 3- and 5-nitrophthalaldehydic acids. The filtrate contains chiefly the 5-nitro-acid. The two acids are separated by fractional crystallisation and by conversion into the copper salts. Phthalaldehydic acid is but little acted on by sulphuric acid, even at 105°, so that the formation of anhydrides during nitration probably occurs after the introduction of the nitro-group.

5-Nitrophthalaldehydic acid, $\text{CHO} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{CO}_2\text{H}$, crystallises from water in yellow leaflets and melts at 159—161°, dissolving readily in ether, alcohol, or acetic acid, sparingly in benzene. Phenylhydrazine gives with it a red precipitate. Concentrated sulphuric acid converts it into an *anhydride*, $\text{C}_6\text{H}_3\text{O}_9\text{N}_2$, crystallising from acetone in small, white, silky needles and melting at 224—226°. The same anhydride is also obtained, mixed with unaltered acid, when the acid is heated at 174°. Oxidation with potassium permanganate in alkaline solution forms 4-nitrophthalic acid. *p*-Nitrobenzaldehyde is obtained on heating the silver salt at 250° under 12 mm. pressure.

3-Nitrophthalaldehydic acid, $\text{C}_8\text{H}_5\text{O}_5\text{N} \cdot \text{H}_2\text{O}$, crystallises from water and shows a variable melting point, but after drying at 100° and crystallising from chloroform, forms aggregates of faintly-yellow needles and melts at 156—157°. Potassium permanganate oxidises it to 3-nitrophthalic acid, and *o*-nitrobenzaldehyde is obtained on heating the silver salt. The *anhydride* melts at 244—248°, or probably higher.

5-Nitrophthalaldehydic acid combines on warming with methyl alcohol to form the *ψ*-methyl ester, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CH(OMe)} \end{smallmatrix} \text{O}$, crystallising from benzene and melting at 101—103°; it is hydrolysed when boiled with water. The true *methyl* ester, prepared by warming the silver salt with methyl iodide, crystallises from a mixture of benzene and light petroleum and melts at 85—86°. Potassium permanganate oxidises it to 2-methyl hydrogen 4-nitrophthalate, crystallising from dry benzene in yellow needles and melting at 140—142°.

3-Nitrophthalaldehydic acid behaves in a similar manner. The *ψ*-methyl ester, prepared by heating the acid with methyl alcohol at 100°, crystallises from methyl alcohol in colourless prisms and melts at 106—108°. The true *methyl* ester, prepared from the silver salt and methyl iodide or by methylating the acid with methyl alcohol and hydrogen chloride in the cold, melts at 145—146°. The true ester is in both cases more stable towards water than the *ψ*-ester. C. H. D.

An Alcohol derived from Coumarin and its Conversion into a Coumarone Derivative. RICHARD STOERMER and ED. OETKER (*Ber.*, 1904, 37, 192—203).—The yield of 4-chloromethylsalicylaldehyde by Behn and Stoermer's method (*Abstr.*, 1901, i, 426) may be increased by hydrolysing the oily by-product, which consists of the ether,

[CHO·C₆H₃(OH)·CH₂]₂O, with gaseous hydrogen chloride in alcoholic ethereal solution.

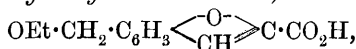
6-Acetoxyethylcoumarin, 6OAc·CH₂·C₆H₃ < $\begin{smallmatrix} \text{O}-\text{CO} \\ \text{CH}:\text{CH} \end{smallmatrix}$, obtained by the action of acetic anhydride and anhydrous sodium acetate on 4-hydroxy-methylsalicylaldehyde and subsequent distillation under reduced pressure, crystallises from alcohol in large, colourless plates melting at 108—109°, dissolves readily in alcohol, chloroform, or acetic acid, and boils at 205—207° under 10 mm. pressure. When boiled with concentrated hydrochloric acid, it yields 6-chloromethylcoumarin,

CH₂Cl·C₆H₃ < $\begin{smallmatrix} \text{O}-\text{CO} \\ \text{CH}:\text{CH} \end{smallmatrix}$, which crystallises from a mixture of benzene and light petroleum in colourless needles melting at 140—141°. When boiled with water, the chloro-derivative is converted into the corresponding alcohol, coumarincarbinol, OH·CH₂·C₆H₃ < $\begin{smallmatrix} \text{O}-\text{CO} \\ \text{CH}:\text{CH} \end{smallmatrix}$, which

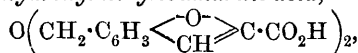
melts at 150°. On oxidation, the carbinol yields coumarinaldehyde in the form of colourless needles melting at 187°; its oxime melts at 223°, and its semicarbazone sinters at 305°, but is not melted at 320°

Coumarin-6-carboxylic acid, CO₂H·C₆H₃ < $\begin{smallmatrix} \text{O}-\text{CO} \\ \text{CH}:\text{CH} \end{smallmatrix}$, obtained by oxidising the aldehyde, melts and decomposes at 267—268°, and the methyl ester crystallises from benzene in colourless needles melting at 174°.

A mixture of mono- and di-bromo-derivatives is obtained when the 6-acetoxyethylcoumarin is brominated in diffused daylight in carbon tetrachloride solution. This mixture, when warmed with alcoholic potash, yields 4-ethoxymethylcoumarilic acid,

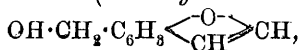


and the ether of 4-hydroxymethylcoumarilic acid,



which may be separated by fractional crystallisation from water. The ethoxy-acid crystallises from a mixture of benzene and light petroleum in pliable needles melting at 163—164° and only sparingly soluble in water; the calcium salt crystallises in plates and is readily soluble in water. Both the ethoxy-acid and the ether of the hydroxy-acid, when warmed with alcoholic hydrogen chloride, yield ethyl 4-chloromethylcoumarilate, C₁₂H₁₁O₃Cl, which crystallises from benzene in monoclinic prisms melting at 65—66°. 4-Hydroxymethylcoumarilic acid, obtained by the action of aqueous potash on the chlorinated ester, forms a colourless, microcrystalline powder very sparingly soluble in water; the calcium salt is readily soluble. The hydroxy-acid, when oxidised with chromic anhydride, yields 1:4-coumarone-dicarboxylic acid, CO₂H·C₆H₃ < $\begin{smallmatrix} \text{O}^- \\ \text{CH} \end{smallmatrix}$ C·CO₂H, as a white powder which is not melted at 310°.

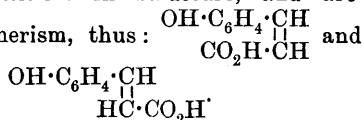
4-Hydroxymethylcoumarone (coumaryl-4-carbinol),



may be obtained by distilling mercurous hydroxymethylcoumarilate under a pressure of 10—15 mm., and is best isolated as its *phenylurethane* derivative, $C_{16}H_{13}O_3N$, which melts at 90° . The alcohol melts at $26-27^\circ$ and distills at $147-150^\circ$ under 12 mm. pressure. An aldehyde, the semicarbazone of which melts at 232° , and an oil, probably 4-methylcoumarone, are also formed during the distillation of the mercurous salt.

J. J. S.

Constitution of Coumarinic Acid. WALTHER BORSCHKE (*Ber.*, 1904, 37, 346—348).—The author has studied the constitution of the two isomeric forms of hydroxycinnamic acid. Coumarinic and coumaric acids are identical in structure, and are regarded as exhibiting *cis-trans*-isomerism, thus:



The formula, representing coumarinic acid as a cyclic anhydride of an ortho-form of *o*-hydroxyphenylacrylic acid, is discarded.

Coumarin was converted into potassium coumarinate and then coupled with phenyldiazonium chloride. Glistening leaflets of benzene azocoumarin melting at 158° were isolated. That the substance thus

obtained has the structure $\text{PhN}_2 \cdot \text{C} \begin{array}{l} \text{CH} \text{---} \text{C} \cdot \text{CH} \cdot \text{CH} \\ \text{CH} \cdot \text{CH} \cdot \text{C} \text{---} \text{O} \text{---} \text{CO} \end{array}$, and not

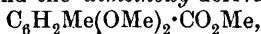
$\text{C}_6\text{H}_4 \begin{array}{l} \text{CH} \cdot \text{C} \cdot \text{N}_2\text{Ph} \\ \text{O} \text{---} \text{CO} \end{array}$, is proved by the formation of benzeneazocoumarin from benzeneazosalicylaldehyde by the Perkin reaction. A. McK.

Ether-esters of β -Resorcylic, Orsellinic, and Orcinolcarboxylic Acids. JOSEF HERZIG and FRANZ WENZEL (*Monatsh.*, 1903, 24, 881—914).—From the results obtained by Herzig and Pollak from gallic acid and pyrogallolcarboxylic acid (*Abstr.*, 1903, i, 89, 346), β -resorcylic, orsellinic, and orcinolcarboxylic acids should readily yield monoether-esters, but should only form diether-esters with difficulty in presence of a large excess of diazomethane, and this is found to be the case.

[With BERNHARD BATSCHA].—*Methyl 2-hydroxy-4-methoxybenzoate*, $\text{OH} \cdot \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{CO}_2\text{Me}$, from β -resorcylic acid and diazomethane, melts at $48-50^\circ$, gives an intense reddish-violet coloration with ferric chloride, and dissolves in dilute potassium hydroxide. Methyl iodide forms *methyl 2:4-dimethoxybenzoate*, which is an oil. The ethyl ether-ester melts at $53-54^\circ$ (compare Perkin, *Trans.*, 1895, 67, 990, and Gregor, *Abstr.*, 1896, i, 171), and dissolves in potassium hydroxide, although less readily than the methyl ether. Ethyl iodide and potassium hydroxide form the *diethyl ether-ester*, which is also oily and yields 2:4-diethoxybenzoic acid on hydrolysis.

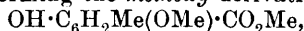
[With P. KURZWEIL].—*Methyl orcinolcarboxylate (methyl 4:6-dihydroxy-2-methylbenzoate)*, $\text{C}_6\text{H}_2\text{Me}(\text{OH})_2 \cdot \text{CO}_2\text{Me}$, from orcinolcarboxylic acid and diazomethane, crystallises from alcohol in long, colourless needles and melts at $98-99^\circ$. The further action of diazomethane

forms the *methoxy*-derivative, melting at 95—97° and dissolving in potassium hydroxide, and the *dimethoxy*-derivative,



short prisms melting at 80—84°, insoluble in potassium hydroxide. On hydrolysis, the two ethers yield the *ether-acid*, decomposing at 169—170°, and the *diether-acid*, decomposing at 178°, respectively.

Methyl orsellinate (methyl 2:6-dihydroxy-4-methylbenzoate) reacts with diazomethane, forming the *methoxy*-derivative,



which crystallises in narrow, white leaflets melting at 63—65°, and the *dimethoxy*-derivative, which was not isolated in a pure state. The *ether-acid* and *diether-acid* melt at 145—146° and 140° respectively.

The oxidation of orceinol to orcein by hydrogen peroxide and ammonia, observed by Zulkowsky and Peters (Abstr., 1890, 1405), does not occur in the case of orcinolcarboxylic acid or its ester, or of the ethers or ester of orsellinic acid. Orsellinic acid, however, yields a violet dye, probably identical with orcein.

[With F. HAISER.]—Methylresorcinol (2:6-dihydroxytoluene) is readily prepared by methylating β -resorcylic acid with sodium and methyl iodide, and acting with hydriodic acid on the resulting 2-methoxy-6-hydroxytoluene-4-carboxylic acid, carbon dioxide being removed; it melts at 116—121° and boils at 264° (uncorr.) (compare Ullmann, Abstr., 1884, 1317). The *benzoyl* derivative crystallises from dilute alcohol and melts at 101—103°. The anhydrous sodium salt reacts with carbon dioxide at 180° under 6 atmospheres pressure, forming methylresorcylic acid, the methyl ester of which melts at 130—132°, but is evidently identical with the ester described by Batscha (Abstr., 1903, i, 491).

[With P. KURZWEIL.]—Methyl iodide and sodium convert orcinolcarboxylic acid into a mixture consisting of a compound soluble in potassium hydroxide, which was not further investigated, and an insoluble compound containing no methoxyl or carboxyl, which seems to be $\text{CO}\langle\begin{smallmatrix} \text{CMe}_2\cdot\text{CMe} \\ \text{CMe}_2-\text{CO} \end{smallmatrix}\rangle\text{CH}$, together with two crystalline compounds, $\text{C}_{11}\text{H}_{14}\text{O}_4$, melting at 115—117°, and $\text{C}_9\text{H}_{12}\text{O}_2$, melting at 160—162°, the investigation of which is not yet completed. C. H. D.

Bismuth Phthalate and Mellitate and Pyrophoric Bismuth. PAUL THIBAUT (*Bull. Soc. chim.*, 1904, [iii], 31, 135—137. Compare Abstr., 1902, i, 290).—When anhydrous bismuth oxide is treated with excess of phthalic acid in presence of boiling water, it is transformed in the course of from 10 to 12 hours into a *bismuth phthalate* having the composition $2\text{Bi}_2(\text{C}_8\text{H}_4\text{O}_4)_3\cdot\text{Bi}_2\text{O}_3$: this crystallises in needles, decomposes at 300°, is dissociated by water, and is insoluble in ordinary solvents, but is decomposed by mineral acids and by alkalis.

Anhydrous bismuth oxide is not acted on by either *iso*- or *meta*-phthalic acid, and the hydrated oxide is not attacked by any of the three phthalic acids.

Warm aqueous solutions of mellitic acid act rapidly on either anhydrous or hydrated bismuth oxide, producing *bismuth mellitate*,

$\text{Bi}_2\text{C}_{12}\text{O}_{12}$, which forms acicular crystals, has a sp. gr. 4.04 at 20° , is insoluble in ordinary solvents, including acetic acid, but is decomposed by mineral acids. When heated under reduced pressure in closed tubes, the salt begins to decompose about 350° , and beyond this temperature evolves carbon dioxide and is converted into a mass of carbonaceous matter containing finely-divided bismuth. This product is slowly attacked by hydrochloric acid and vigorously by nitric acid, and when thrown into the air spontaneously inflames, producing vapours of bismuth oxide. No mellitic acid sublimes during the pyrogenic decomposition of bismuth mellitate. T. A. H.

Halogen Substitution Products of α - and γ -Truxillic Acid.
RUDOLPH KRAUSS (*Ber.*, 1904, 37, 216—224. Compare Abstr., 1902, i, 785).—*Methyl dibromo- α -truxillate*, prepared by brominating methyl α -truxillate, crystallises from methyl alcohol in white needles and melts at 172° .

Ethyl hexachloro- α -truxillate, $\text{C}_{16}\text{H}_8\text{Cl}_6(\text{CO}_2\text{Et})_2$, prepared by chlorinating ethyl α -truxillate at 50° , melts at 178° , whilst *methyl hexachloro- α -truxillate* crystallises in needles and melts at 215° .

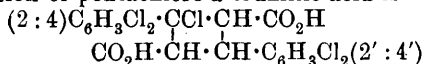
Hexachloro- α -truxillic acid, prepared by hydrolysing the latter compound, separates from alcohol in needles and melts at 316° ; its solution in sodium carbonate does not reduce permanganate. On distillation, it yields 2:4- β -trichlorocinnamic acid, which forms yellow needles, melts at 173° , and reduces permanganate. That the latter acid was not an α -acid was proved by its behaviour on oxidation with potassium permanganate, since there was no evidence for the formation of dichlorobenzaldehyde when an insufficiency of the oxidising agent was used, the acid obtained being 2:4-dichlorobenzoic acid, which crystallises in needles and melts at 156 — 158° .

Ethyl pentachloro- α -truxillate, prepared by chlorinating ethyl- α -truxillate on a boiling water-bath, melts at 142° . *Methyl pentachloro- α -truxillate* forms needles and melts at 176° . *Pentachloro- α -truxillic acid* separates from alcohol in small needles and melts at 274° ; when distilled, it forms a mixture of dichloro- and trichloro-cinnamic acids, which on oxidation yields 2:4-dichlorobenzoic acid.

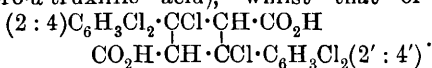
Methyl dibromo- γ -truxillate, prepared by brominating methyl- γ -truxillate, melts at 163° . *Dibromo- γ -truxillic acid* separates from alcohol in tiny needles and melts at 280° ; when distilled, it forms *p*-bromocinnamic acid. *Methyl p*-bromocinnamate crystallises in needles and melts at 79 — 80° . *p*-Bromobenzoic acid is formed by the oxidation of *p*-bromocinnamic acid by permanganate. *Methyl hexachloro- γ -truxillate* separates from alcohol in tiny needles and melts at 180 — 182° . *Hexachloro- γ -truxillic acid* separates from alcohol in small needles, melts at 285° , and does not reduce permanganate. When distilled, it forms 2:4- β -trichlorocinnamic acid, since the oxidation of the product yields 2:4-dichlorobenzoic acid.

The corresponding halogen derivatives of the stereoisomeric α - and γ -truxillic acids are accordingly very similar; the derivatives of the γ -acid have lower melting points than the corresponding derivatives of the α -acid.

The constitution of pentachloro- α -truxillic acid is



(2:4:2':4'- β -chloro- α -truxillic acid), whilst that of hexachloro- α -truxillic acid is



A. McK.

Veratroylformic Acid and its Reduction. L. VANZETTI (*Atti R. Accad. Lincei*, 1903, [v], 12, ii, 629—635).—The preparation of veratroylformic acid from dimethylolivil (Körner and Vanzetti, *Abstr.*, 1903, i, 430) is described: it is best purified by means of its bisulphite derivative, crystallises from ether in small, white nodules composed of flexible needles, and melts at 138—139° to a dark brown liquid. In structure, it is 3:4-dimethoxybenzoylformic acid, as shown by its formation on oxidising methyleugenol (Tiemann and Matmoto, *Abstr.*, 1878, 503) and methylisoeugenol (Ciamician and Silber, *Abstr.*, 1890, 966). On fusion with an alkali hydroxide, it is converted into protocatechuic acid, and with chromic acid in acetic acid solution it yields veratric acid. When heated above 200°, it loses carbon dioxide, giving a small quantity of methylvanillin. The *potassium, silver, barium, lead, and copper* salts are described.

On reduction with sodium amalgam, veratroylformic acid gives 3:4-dimethoxymandelic acid, $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$, which crystallises from benzene in white, lustrous plates, melts at 105°, and slowly decomposes on exposure to light, giving a resin containing methylvanillin; it undergoes a slight decomposition in the same sense when crystallised from various solvents. The *alkali* salts crystallise from alcohol, and the *silver* salt darkens in the air; the *lead and copper* salts are also described.

W. A. D.

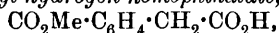
Esterification of Unsymmetrical Di- and Poly-basic Acids.

XII. Esterification of Phthalonic and Homophthalic Acids. RUDOLF WEGSCHEIDER and ARTHUR GLOGAU (*Monatsh.*, 1903, 24, 915—958. Compare *Abstr.*, 1900, i, 657; 1902, i, 617, 620).—Methyl alcohol and hydrogen chloride convert phthalonic acid into methyl phthalonate, $\text{C}_{11}\text{H}_{10}\text{O}_5$, crystallising from methyl alcohol in rhombic plates [$a:b:c=0.9137:1:1.0106$] and melting at 66—68° (compare Zincke and Breuer, *Abstr.*, 1885, 269), and *methyl hydrogen phthalonate*, $\text{C}_{10}\text{H}_8\text{O}_5\cdot\text{H}_2\text{O}$, melting at 79—81°; the anhydrous ester melts at 74—85° undergoing partial decomposition. The same esters are obtained when phthalonic acid is heated with methyl alcohol at 100°, or when silver phthalonate or potassium hydrogen phthalonate reacts with methyl iodide. Sulphuric acid and methyl alcohol convert phthalonic acid into phthalic acid and methyl phthalate. Diazomethane forms the same esters. The partial hydrolysis of methyl phthalonate with hydrogen chloride or potassium hydroxide also forms the same methyl hydrogen phthalonate, and all attempts to prepare an isomeride were thus unsuccessful.

Homophthalic acid reacts with hydrogen chloride and methyl alcohol, forming methyl homophthalate and *b-methyl hydrogen homo-*

phthalate, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$, crystallising from ether in thin tablets and melting at $96-98^\circ$, dissolving readily in ether, methyl alcohol, or benzene, sparingly in light petroleum. The same ester is obtained on heating homophthalic acid or homophthalic anhydride with methyl alcohol, and is probably present in the mixture obtained by the action of sodium methoxide on homophthalic anhydride in methyl alcohol solution.

The isomeric *a-methyl hydrogen homophthalate*,



is obtained on heating potassium hydrogen homophthalate with methyl iodide, by the action of diazomethane on homophthalic acid, and by the partial hydrolysis of methyl homophthalate with potassium hydroxide, and in small quantity from silver homophthalate and methyl iodide. It crystallises from benzene in transparent tablets and melts at $143-145^\circ$, dissolving readily in alcohol or ether, sparingly in light petroleum or cold water.

b-Ethyl hydrogen homophthalate is prepared in similar manner (compare Wislicenus, Abstr., 1886, 879).

The *b*-methyl ester reacts with concentrated ammonium hydroxide, forming phenylacetamide-*o*-carboxylic acid, which is converted by bromine and potassium hydroxide into *benzylamine-o-carboxylic acid*, $\text{C}_8\text{H}_9\text{O}_2\text{N}$, melting at $217-220^\circ$ after repeated recrystallisation from water. On heating for some time slightly above the melting point, phthalimidine is formed by loss of water.

The *a*-methyl ester reacts slowly with ammonium hydroxide, forming *benzamide-2-acetic acid*, $\text{NH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, decomposing slightly at 190° , completely at 230° .
C. H. D.

Isomeric *m*-Nitrobenzaloximes. HEINRICH GOLDSCHMIDT (*Ber.*, 1904, 37, 180—184. Compare Abstr., 1890, 1262; and Ciamician and Silber, this vol., i, 162).—It is shown that Ciamician and Silber's compound melting at $95-100^\circ$ is a mixture of the *syn*- and *anti*-compounds. The pure *syn*-oxime, obtained by the method already described, melts at $118-119^\circ$, which is practically the same temperature ($121-122^\circ$) as the *anti*-compound. This is due to the fact that the *syn*-compound, during the heating, becomes transformed into the *anti*-. If the *syn*-compound is plunged into a bath at 90° or at any higher temperature, it melts, then solidifies, and afterwards melts at $118-119^\circ$. The transformation is also brought about to a certain extent when the *syn*-compound is crystallised from benzene. The configurations are in agreement with the relative strengths of the oximes (*Ber.*, 1895, 28, 2019), and also with the decomposition of the acetate of the *syn*-oxime into acetic acid and a nitrile (Hantzsch, Abstr., 1894, i, 331).

syn-Aldoximes are more readily esterified than the *anti*-isomerides, as was to be expected from the behaviour of *cis*- and *trans*-modifications of monobasic acids [compare Sudborough and Lloyd, Trans., 1898, 73, 81].
J. J. S.

Synthesis of Aromatic Aldehydes. F. BODROUX (*Compt. rend.*, 1904, 138, 92—94).—Magnesium phenyl bromide reacts with ethyl orthoformate on prolonged boiling and subsequent treatment with

hydrochloric acid to form benzaldehyde, according to the following equations: $\text{MgPhBr} + \text{OEt} \cdot \text{CH}(\text{OEt})_2 = \text{Mg}(\text{OEt})\text{Br} + \text{CHPh}(\text{OEt})_2$, $\text{CHPh}(\text{OEt})_2 + \text{H}_2\text{O} + \text{HCl} = 2\text{CH}_3 \cdot \text{CH}_2 \cdot \text{OH} + \text{HCl} + \text{CHPhO}$, and the yield is 90 per cent. of that required by theory.

A yield of 65 per cent. of *p*-tolualdehyde can similarly be obtained from magnesium *p*-tolyl bromide and ethyl orthoformate, whilst only 20 per cent. of phenylacetaldehyde is obtained by the action of magnesium benzyl chloride on ethyl orthoformate.

Iodoform and bromoform react energetically with magnesium phenyl bromide at the ordinary temperature to yield, among other products, triphenylmethane; the yield is, however, never greater than one-fourth of the theoretical. M. A. W.

Acidimetry of the Hydroxyaldehydes. HANS MEYER (*Monatsh.*, 1903, 24, 832—839).—Astruc and Murco have shown (*Abstr.*, 1901, i, 66) that certain hydroxyaldehydes react as monobasic acids, and may be titrated with alkali hydroxides in aqueous or alcoholic solution. Piperonal, which does not contain a hydroxyl group, was erroneously included by them, and is found to be entirely neutral. *p*-Hydroxybenzaldehyde and protocatechuic aldehyde behave as monobasic acids, requiring one equivalent of alkali for neutralisation, and vanillin requires only slightly less. *o*-Hydroxybenzaldehyde requires less alkali for neutralisation, and *m*-hydroxybenzaldehyde much less, *iso*Vanillin is neutral (Wegscheider, *Abstr.*, 1883, 190), and the proportions necessary to obtain a good yield in the methylation of protocatechuic aldehyde are given. C. H. D.

Ethers and Homologues of Phloroglucinolaldehyde [2:4:6-Trihydroxybenzaldehyde]. JOSEF HERZIG and FRANZ WENZEL (*Monatsh.*, 1903, 24, 857—880. Compare *Abstr.*, 1901, i, 473; 1902, i, 463).—[With E. KERÉNYI].—No ether is obtained when hydrogen chloride is passed into a solution of 2:4:6-trihydroxybenzaldehyde or its aldimide in methyl alcohol, condensation taking place. Diazomethane forms the dimethyl ether, 6-hydroxy-2:4-dimethoxybenzaldehyde, which crystallises from light petroleum in white plates and melts at 70—71°, dissolving readily in organic solvents, insoluble in water. 2:6-Dihydroxy-4-methoxybenzaldehyde could not be prepared by direct methylation, but is obtained when hydrogen cyanide and hydrogen chloride react with phloroglucinol methyl ether and the resulting imide is boiled with water, and crystallises in white needles 3—4 cm. long, decomposing at 170°. Diazomethane forms the dimethyl ether, but a third methyl group cannot thus be introduced. Sodium and methyl iodide, however, react forming 2:4:6-trimethoxybenzaldehyde, melting at 118°.

2:4:6-Trimethoxybenzaldehyde does not form a coumarin derivative with acetic anhydride, but yields a *triacetyl* derivative crystallising in plates and melting at 122—123°, and a *penta-acetyl* derivative melting at 155—156°.

[With H. GEHRINGER].—2:4:6-Trimethoxybenzaldehyde may also be obtained by the action of hydrogen cyanide and hydrogen chloride on phloroglucinol trimethyl ether, the aldimide thus formed being boiled with water. The *oxime*, $\text{C}_6\text{H}_2(\text{OMe})_3 \cdot \text{CH} \cdot \text{NOH}$, crystallises

from methyl alcohol in white needles and melts at 201—203°. 2:4:6-Trimethoxybenzaldehyde condenses with malonic acid in presence of pyridine, forming 2:4:6-trimethoxycinnamic acid, $C_6H_2(OMe)_3 \cdot CH:CH \cdot CO_2H$, crystallising from methyl alcohol in yellowish-white, silky needles melting and decomposing at 218°. Methyl iodide forms the *methyl ester*, white needles melting at 134—135°.

Trimethoxybenzaldehyde condenses with acetone in presence of sodium hydroxide, forming 2:4:6-trimethoxybenzylideneacetone, $C_6H_2(OMe)_3 \cdot CH:CH \cdot COMe$, crystallising from light petroleum in yellow scales, softening at 112°, and melting at 118—120°. Condensation with formaldehyde forms white, hygroscopic needles of *methylenebis-2:4:6-trimethoxybenzaldehyde*, $CH_2[C_6H_2(OMe)_3 \cdot CHO]_2$, melting at 154—155°.

Potassium permanganate oxidises phloroglucinolaldehyde trimethyl ether in alkaline solution to 2:4:6-trimethoxybenzoic acid. The *ethyl ester* crystallises from light petroleum in long, thin needles and melts at 77—78°.

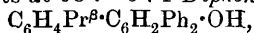
[With E. KERÉNYI.]—*Methylphloroglucinolaldehyde* [2:4:6-trihydroxy-3-methylbenzaldehyde], $C_6HMe(OH)_3 \cdot CHO$, prepared from methylphloroglucinol by Gattermann's synthesis, crystallises from water with $\frac{1}{2}H_2O$, and after drying at 100° dissolves readily in alcohol, glacial acetic acid, or ethyl acetate, sparingly in ether or water, insoluble in benzene, light petroleum, or chloroform. The *oxime* forms slightly yellow crystals and begins to decompose at 140°, melting to a black mass at 170°. The *penta-acetyl* derivative, $C_6HMe(OAc)_3 \cdot CH(OAc)_2$, crystallises from alcohol in white leaflets and melts at 144—145°.

Dimethylphloroglucinolaldehyde [2:4:6-trihydroxydimethylbenzaldehyde], $C_6Me_2(OH)_3 \cdot CHO$, prepared in a similar manner from dimethylphloroglucinol, crystallises from ethyl acetate in almost white crystals and decomposes at 190°. The *oxime* forms colourless crystals, insoluble in benzene, light petroleum, or chloroform, dissolving readily in ethyl acetate, ether, or methyl alcohol, and melts at 168°. The *penta-acetyl* derivative, $C_6Me_2(OAc)_3 \cdot CH(OAc)_2$, forms white leaflets and melts at 152—153°.

C. H. D.

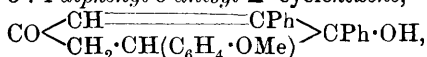
Δ^2 -Ketocyclohexene Derivatives. JAMES B. GARNER (*Amer. Chem. J.*, 1904, 31, 143—153).—4-Hydroxyketo-3:4-diphenyl-5-cumyl-

Δ^2 -cyclohexene, $CO \begin{matrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CH}(C_6H_4 \cdot CHMe_2) \end{matrix} \text{CPh} \cdot OH$, obtained by the condensation of benzoin with cumylideneacetone in presence of sodium ethoxide, crystallises in long, slender, white needles, melts at 231°, and is readily soluble in hot benzene, glacial acetic acid, or chloroform; its *oxime* melts at 221—223°. When this ketone is boiled with excess of acetic anhydride or acetyl chloride, it is converted into 3:4-diphenyl-5-cumylphenyl acetate, which crystallises in groups of long needles and melts at 98°. 3:4-Diphenyl-5-cumylphenol,



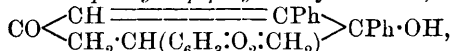
prepared by hydrolysing the acetate, forms white needles, melts at 155° and is readily soluble in chloroform, benzene, or ether.

4-Hydroxyketo-3 : 4-diphenyl-5-anisyl- Δ^2 -cyclohexene,



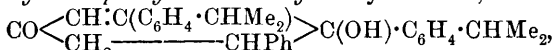
prepared by the condensation of benzoin with anisylideneacetone, crystallises in needles, melts at 233.5° , is soluble in hot benzene or chloroform, and gives a red coloration with concentrated sulphuric acid; its *oxime* melts at 196° . 3 : 4-Diphenyl-5-anisylphenol is a crystalline substance which melts at $159-160^\circ$, and is readily soluble in ether, benzene, chloroform, or acetic acid; its *acetate* melts at $141-142^\circ$.

4-Hydroxyketo-3 : 4-diphenyl-5-piperyl- Δ^2 -cyclohexene,



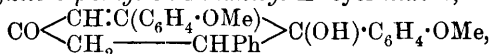
formed by the condensation of benzoin with piperonyleneacetone, crystallises in slender, white, lustrous needles, melts at 240° , is soluble in hot chloroform, and sparingly so in hot benzene or alcohol; its *oxime* melts at $190-191^\circ$.

4-Hydroxyketo-5-phenyl-3 : 4-dicumyl- Δ^2 -cyclohexene,



obtained by the condensation of cumino in with benzylideneacetone, crystallises from glacial acetic acid, melts at 214° , and is soluble in ethyl acetate, chloroform, or hot benzene; its *oxime* melts at 208° . 5-Phenyl-3 : 4-dicumylphenol crystallises in large, thin plates, melts at 137° , and is soluble in ethyl acetate, benzene, chloroform, or ether; its *acetate* melts at 122° .

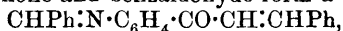
4-Hydroxyketo-5-phenyl-3 : 4-dianisyl- Δ^2 -cyclohexene,



prepared by the condensation of aniso in with benzylideneacetone, crystallises in white needles, melts at 207° , and is soluble in benzene, alcohol, acetic acid, or chloroform. The 1 : 5-diketone, formed as the first product of this reaction, melts at about $168-174^\circ$. E. G.

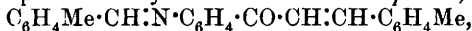
Behaviour of *p*-Aminoacetophenone towards Aldehydes. MAX SCHOLTZ and L. HUBER (*Ber.*, 1904, 37, 390—397).—*p*-Aminoacetophenone contains two groups which are reactive towards aldehydes, the amino-group undergoing condensation in alcoholic solution, and the methyl group adjoining carbonyl condensing in presence of potassium hydroxide. Most aromatic aldehydes undergo both condensations simultaneously in presence of potassium hydroxide, but in the case of aldehydes containing phenolic hydroxyl, the addition of alkali is without effect, only the amino-condensation taking place.

p-Aminoacetophenone and benzaldehyde form a compound,

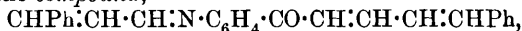


crystallising from pyridine in yellow needles and from glacial acetic acid in red needles, both forms melting at $143-144^\circ$. Boiling dilute hydrochloric acid hydrolyses it to *o*-benzylidene-*p*-aminoacetophenone hydrochloride, $\text{CHPh} \cdot \text{CH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_3\text{Cl}$, crystallising in colourless needles, decomposed by water or by heat. *p*-Benzylideneaminoaceto-

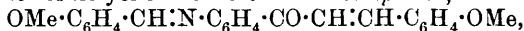
phenone, $\text{CHPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_3$, from *p*-aminoacetophenone and benzaldehyde in neutral solution. crystallises from alcohol in colourless needles and melts at 96° . *p*-Tolualdehyde and *p*-aminoacetophenone in presence of potassium hydroxide form the *compound*,



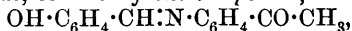
crystallising from pyridine in yellow needles and melting at 188° ; with hydrochloric acid, it forms $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_3\text{Cl}$. *p*-Aminoacetophenone and piperonal in alkaline solution form the *compound*, $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_3\cdot\text{O}_2\cdot\text{CH}_2$, crystallising from pyridine in yellow needles and melting at 189° . Acetic acid removes 1 mol. of piperonal on warming, yielding the *compound*, $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, which forms red needles melting at $198-200^\circ$. The *isomeride*, $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_3$, is formed by the condensation of *p*-aminoacetophenone with piperonal in neutral solution, and melts at 147° . Cinnamaldehyde forms yellow needles of the *compound*,



melting at 191° . Cuminaldehyde forms yellow needles of the *compound*, $\text{C}_6\text{H}_4\text{Pr}\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\text{Pr}$, melting at 128° ; anisaldehyde forms yellow leaflets of the *compound*,



melting at 191° . The condensation products from *m*- and *p*-nitrobenzaldehydes, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, crystallise from pyridine in felted, yellow needles melting at 195° , and brick-red, microscopic needles melting at $191-193^\circ$, respectively. Salicylaldehyde and *p*-aminoacetophenone, with or without the addition of potassium hydroxide, form only the *compound*,



crystallising from alcohol in glistening, orange needles and melting at 116° . *p*-Hydroxybenzaldehyde reacts in similar manner, the product melting at 209° . Vanillin also yields only the *compound*,



which forms yellow (or red) needles melting at 167° . In alkaline solution, furfuraldehyde forms an oil which is converted into the *compound*, $(\text{C}_4\text{H}_3\text{O}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$, H_2SO_4 , by cold dilute sulphuric acid. Formaldehyde and *p*-aminoacetone in neutral solution form the *compound* $\text{CH}_2(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_3)_2$, crystallising from alcohol in colourless needles and melting at 188° . C. H. D.

Additive Compounds derived from *o*-Benzoquinone. C. LORING JACKSON and HORACE C. PORTER (*Amer. Chem. J.*, 1904, 31, 89—119. Compare Abstr., 1903, i, 266).—Tetrabromo-*o*-quinone readily unites with various substances with the formation of additive compounds. When it is left in contact with such a substance for several days at the ordinary temperature, the product consists of 2 mols. of tetrabromo-*o*-quinone combined with 1 mol. of the other substance. These compounds crystallise in white needles or prisms and are stable at the ordinary temperature, but are decomposed by heat with formation of hexabromo-*o*-quinocatechol ether; they are all

soluble in solution of sodium hydroxide. The following is a list of these *compounds*, designated as α -compounds, and the temperatures at which they suffer decomposition: $2C_6O_2Br_4 \cdot H_2O$, $190-200^\circ$; $2C_6O_2Br_4 \cdot MeOH$, $178-182^\circ$; $2C_6O_2Br_4 \cdot CH_2Ph \cdot OH$, $165-170^\circ$; $2C_6O_2Br_4 \cdot CH_3 \cdot CO_2H$, $220-230^\circ$. When the methyl alcohol compound is heated with strong hydrochloric acid at 100° for 30 hours, it yields a compound melting at $185-187^\circ$, which is probably tetrabromocatechol, together with chloroform, chlorine, and possibly bromine. By the action of hydrobromic acid on the benzyl alcohol compound, benzylidene bromide, bromine, and probably benzyl bromide and tetrabromocatechol are produced; hydrochloric acid acts in a similar manner. If the benzyl alcohol compound is boiled with sulphuric acid of sp. gr. 1.38, hexabromo-*o*-quinocatechol ether is obtained.

Another series of compounds, termed β -compounds, is obtained from the α -compounds. The methyl alcohol β -compound is formed when the α compound is boiled with methyl alcohol, whilst the water and benzyl alcohol compounds are produced by the action of acetic anhydride and dry sodium acetate on the corresponding α -compounds. These β -compounds crystallise in white, polygonal plates, are very stable, and melt without undergoing decomposition. The following are the *compounds* which have been prepared, and their melting points: $2C_6O_2Br_4 \cdot MeOH$, 261° ; $2C_6O_2Br_4 \cdot CH_2Ph \cdot OH$, $216-217^\circ$; $2C_6O_2Br_4 \cdot H_2O$, 222° .

The first product of the action of methyl alcohol on tetrabromo-*o*-benzoquinone is not the α -compound, but a *substance*, probably $3C_6O_2Br_4 \cdot MeOH$, which crystallises in small, red prisms and melts at $192-193^\circ$. The *acetyl* derivative of the methyl alcohol β -compound, $2C_6O_2Br_4 \cdot CH_3 \cdot CO_2Me$, crystallises in needles and melts at 249° . By the action of acetic anhydride on the benzyl alcohol β -compound, a *substance*, $C_6O_2Br_4 \cdot CH_3 \cdot CO_2 \cdot CH_2Ph$, is produced, which forms greyish-white crystals and melts at $208-209^\circ$. When the benzyl alcohol α -compound is reduced with zinc and acetic acid, a *compound*, $2C_6H_2O_2Br_4 \cdot CH_2Ph \cdot OH$, is obtained, which crystallises in pale yellow needles, melts at $273-274^\circ$, and yields a *triacetyl* derivative melting at $275-280^\circ$.

Toluene and acetophenone unite with tetrabromo-*o*-quinone forming two red *substances*, $C_6O_2Br_4 \cdot C_6H_5Me$ and $C_6O_2Br_4 \cdot C_6H_5 \cdot COMe$, melting at $70-75^\circ$ and $50-60^\circ$ respectively, which, on exposure to air, gradually lose the volatile constituent; it therefore appears that these substances are merely tetrabromo-*o*-quinone with toluene or acetophenone of crystallisation. When tetrabromo-*o*-quinone is boiled with acetophenone, triphenylbenzene is produced.

It has been stated previously (Jackson and Koch, Abstr., 1901, i, 597-598) that by the action of glacial acetic acid on tetrabromo-*o*-quinone, hexabromo-*o*-quinocatechol is produced, but it is now found that this substance was formed indirectly by the action of alcohol on the crude product. The white additive compound of acetic acid obtained by Jackson and Koch (*loc. cit.*) is apparently related to the β -series, since it is formed when the α -compound is heated with acetic acid,

When tetrabromo-*o*-benzoquinone is heated at 130—150°, it undergoes decomposition with formation of hexabromo-*o*-quinocatechol ether and a white substance melting at 180—190°. The quinone is decomposed by boiling water with production of hydrogen bromide and hexabromo-*o*-quinocatechol ether. Fuming nitric acid dissolves the quinone forming a purple coloured solution from which, on diluting with water, the quinone is reprecipitated unchanged. E. G.

2-Substitution Derivatives of Anthraquinone. FELIX KAUFLE (Ber., 1904, 37, 59—66).—The following compounds were prepared from 2-aminoanthraquinone through the diazo-reaction (compare this vol., i, 207). 2-Iodoanthraquinone crystallises from alcohol in light yellow needles, melts at 175—176°, and boils at 290—300° under 15 mm. pressure; on nitration, it gives remarkably stable nitro-derivatives, and does not lose iodine when boiled with methyl-alcoholic potassium methoxide. 2-Bromoanthraquinone, prepared by converting anthraquinone-2-diazonium bromide into its perbromide and decomposing this at 200°, crystallises from amyl alcohol and melts at 204—205°; Graebe and Liebermann (*Annalen*, 1870, Supt.-Band., 7, 279) have described 2-bromoanthraquinone as melting at 187°. 2-Chloroanthraquinone melts at 208—209°, not at 204°, as stated by Graebe and Rée (*Trans.*, 1886, 49, 531). 2-Nitroanthraquinone, prepared by decomposing anthraquinone-2-diazonium nitrate with sodium copper nitrite according to Hantzsch and Blagden's method (*Abstr.*, 1900, i, 704), crystallises from glacial acetic acid in bright yellow, lustrous needles, melts at 184—185°, and boils without decomposing; on reduction, it regenerates 2-aminoanthraquinone. 2-Nitroanthraquinone differs from the 1-nitro-compound in not being attacked by boiling aniline or *p*-toluidine, although resembling it in undergoing conversion into 2-methoxyanthraquinone when heated with methyl-alcoholic potassium methoxide; the product crystallises from alcohol in long, bright-yellow needles and begins to sublime at about 100°. W. A. D.

Anthraquinone-1-sulphonic Acids. ROBERT E. SCHMIDT (Ber., 1904, 37, 66—72).—A claim for priority for the discovery that on sulphonating anthraquinone in presence of mercury or its salts, α - and not β -sulphonic acids are obtained (compare Iljinsky, this vol., i, 176); the process has been patented by Friedrich Bayer & Co. Details are given for preparing anthraquinone-1-sulphonic acid and 1:5- and 1:8-disulphonic acids both by direct sulphonation and by the action of sodium sulphite on 1-nitro, 1:5-, and 1:8-dinitroanthraquinones. The latter process is also employed for preparing anthraquinone-1:6- and 1:7-disulphonic acids from Claus's α - and β -nitroanthraquinonesulphonic acids respectively.

When the 1-anthraquinonesulphonic acids are heated at a high temperature with ammonia or primary amines, the corresponding amino- or alkylamino-anthraquinones which have already been described are obtained (compare *Abstr.*, 1903, i, 498, 839). When heated with methyl-alcoholic potassium hydroxide, the analogous methoxyanthraquinones are produced, and with a solution of potassium

phenoxide in an excess of phenol, anthraquinone-1-sulphonic acid gives the hitherto unknown *phenoxyanthraquinone*.

On reduction with zinc dust and ammonia, anthraquinone-1-sulphonic acid gives anthracene-1-sulphonic acid, which, on fusion with potassium hydroxide, is converted into *α-anthrol*. The latter crystallises from acetic acid on diluting with water in yellow leaflets and melts at 152°.

On oxidation with 80 per cent. sulphuric anhydride at 30—35°, the same sulphonic acid gives a new *purpurinsulphonic acid* (1:2:4-trihydroxyanthraquinone-5- or -8-sulphonic acid). On nitration, the 1-sulphonic acid gives a mixture of 5-nitro- and 8-nitro-anthraquinone-1-sulphonic acids, which are easily separated; the former crystallises from the concentrated acid and the latter separates on diluting with water. On reducing the nitro-acids with aqueous sodium sulphide, the sodium salts of 5- and 8-aminoanthraquinone-1-sulphonic acids are obtained; these can be diazotised and coupled with phenols and with amines. On heating the aminoanthraquinonesulphonic acids with lime-water at a high temperature, 5- and 8-amino-1-hydroxyanthraquinones are obtained; with methylamine, 1-methylamino-5- and -8-aminoanthraquinones are produced. 5- and 8-Methylaminoanthraquinone-1-sulphonic acids are obtained by heating the foregoing nitro-sulphonic acids with aqueous methylamine at 50—70°; at a higher temperature (150—170°), 1:5- or 1:8-dimethyldiaminoanthraquinones are the products.

W. A. D.

Action of Nitric Acid on Cyclic Ketones. I. Action of Nitric Acid on the Ketones, $C_{10}H_{16}O$, of the Terpene Series. MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 953—962).—The action of nitric acid of sp. gr. 1.075 and 1.1 on fenchone in sealed tubes at 120—130° leaves nearly the whole of the fenchone unchanged, only small quantities of the following two products being obtained: (1) a *secondary nitrofenchone*, $C_{10}H_{15}(NO_2)O$, which is soluble in alkali hydroxide solution and separates from light petroleum solution in long, thin needles melting at 86—87°; the nitro-group is reduced to NH_2 by means of tin and hydrochloric acid.

(2) A *tertiary nitrofenchone*, probably $\begin{array}{c} CH_2 \cdot CH - CMe \cdot NO_2 \\ | \quad \quad | \\ | \quad CMe_2 \quad | \\ | \quad \quad | \\ CH_2 \cdot CH - CO \end{array}$, which is

insoluble in alkali hydroxide solution and separates from light petroleum solution in monoclinic, pearly scales or prisms melting at 96.5—97.5°. With tin and hydrochloric acid, it yields a small quantity of the amino-compound, together with the corresponding *hydroxyfenchone*, $C_{10}H_{16}O \cdot OH$, which has the sp. gr. 1.0071 at 25°/0°, and n_D 1.4636 at 25°; it is readily soluble in ether, but only slightly so in water.

The action of nitric acid of sp. gr. 1.075 on pulegone at 80—90° gives products soluble, and others insoluble, in alkali hydroxide solution. Of the latter, four were isolated: (1) a compound $C_{10}H_{15}O \cdot NO_2$, which melts at 123° and yields the corresponding amino-derivative on reduction, and (2) three compounds of the

composition $C_{10}H_{16}O(NO_2)_2$, and melting at $96-98^\circ$, $84-86^\circ$, and $64-72^\circ$ respectively; the one melting at $84-86^\circ$ is obtained also by the action of nitrogen peroxide on a light petroleum solution of pulegone.

With nitric acid of sp. gr. 1.075, dihydrocarvone acts readily at 80° and carvenone at $85-90^\circ$ yielding nitro-derivatives; the unattacked portions do not undergo isomeric change.

From these results and those previously obtained (Abstr., 1896, i, 177), the author draws the following conclusions: (1) the ketones, $C_{10}H_{16}O$, of the terpene series having a saturated character—camphor and fenchone—react with dilute nitric acid with comparative difficulty. The presence of the grouping $-CHMe$ facilitates the action, fenchone reacting more readily than camphor. (2) Those ketones of the terpene series which have an unsaturated character react very readily with dilute nitric acid; with pulegone, combination takes place at the double linking. (3) Under the conditions employed in the author's experiments, dilute nitric acid does not bring about isomeric change in cyclic ketones. (4) In general, cyclic ketones behave towards dilute nitric acid in the same way as towards hydrocarbons.

T. H. P.

Chemically Pure α - and β -Ionones, their Separation, and Hydrogen Sulphite Compounds. PHILIPPE CHUIT (*Chem. Centr.*, 1904, i, 280—281; from *Rev. gén. Chim. pure appl.*, 1903, 6, 422—435).—The oxime of ψ -ionone, prepared in the ordinary way, boils at $185-190^\circ$ under 16 mm. and at $190-195^\circ$ under 20 mm. pressure, and it has the sp. gr. 0.938. By treating the oxime with phosphoric acid of sp. gr. 1.742 (compare Abstr., 1902, i, 722), a product boiling at $172-178^\circ$ under 175 mm. pressure is obtained; the main portion of the liquid boils at $174-175^\circ$ and consists for the most part of α -iononeoxime together with a small quantity of β -iononeoxime. By the action of a 70 per cent. solution of sulphuric acid on ψ -iononeoxime at the ordinary temperature, almost pure β -ionone is obtained. The isomeric change is not so readily effected by means of the phenylhydrazone.

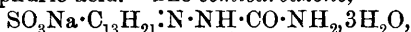
In order to separate α - and β -ionone sodium hydrogen sulphites, the former is salted out by adding sodium chloride to the warm solution of these compounds. The α -compound separates in leaflets which have a nacreous lustre. The β -compound remains in solution or when present in large quantity separates as an oil; on evaporation small crystals are formed.

α -Ionone sodium hydrogen sulphite, $C_{13}H_{21}O \cdot SO_3Na, 1\frac{1}{2}H_2O$, crystallises from water in white leaflets or from alcohol in monoclinic rhombs, is readily soluble in hot alcohol, only slightly so in ethyl acetate, and insoluble in benzene; the ketone group of the ionone is not combined with the sulphite group.

The oxime of α -ionone sodium hydrogen sulphite is readily soluble in water and appears to yield the free oxime when distilled from an alkaline solution with steam. When α -ionone oxime is dissolved in sodium hydrogen sulphite solution, α -ionone sodium hydrogen sulphite and not the oxime compound is formed. The *semicarbazone sodium*

hydrogen sulphite, $\text{SO}_3\text{Na}\cdot\text{C}_{13}\text{H}_{21}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, crystallises from boiling alcohol in slender, white needles and is readily soluble in water; by the action of sodium hydroxide, it appears to form the free semicarbazone of α -ionone and not α -ionone itself. Dilute sulphuric acid precipitates the free acid from its aqueous solution; it forms white leaflets and melts and decomposes at 203° . The *phenylhydrazone* of α -ionone sodium hydrogen sulphite appears to form α -ionone hydrazone when treated with sodium hydroxide; the latter does not dissolve in boiling sodium hydrogen sulphite solution.

When α -ionone sodium hydrogen sulphite is evaporated with a 50 per cent. solution of sulphuric acid in a vacuum at $30\text{--}35^\circ$, a residue is left which is soluble in ethyl acetate but insoluble in benzene. The solution yields a syrupy residue which has a strong acid reaction and the sp. gr. 1.21 at 15° ; the *sodium salt*, $\text{C}_{13}\text{H}_{21}\text{O}\cdot\text{SO}_3\text{Na}$, forms regular, transparent crystals and is very sparingly soluble in ethyl acetate. The *potassium salt* is also anhydrous. A second stable acid, $\text{C}_{13}\text{H}_{21}\text{O}\cdot\text{SO}_3\text{H}\cdot 3\text{H}_2\text{O}$, may be prepared by evaporating an aqueous solution of α -ionone sodium hydrogen sulphite with sulphuric acid to dryness on the water-bath or by heating the salt with a 50 per cent. solution of sulphuric acid for a short time at 60° ; it is readily soluble in alcohol, ether, ethyl acetate, or water, but less so in warm benzene, and melts and decomposes at $80\text{--}88^\circ$. By the action of sodium hydroxide on this acid, α -ionone is not formed, but only the *sodium salt*, $\text{C}_{13}\text{H}_{21}\text{O}\cdot\text{SO}_3\text{Na}\cdot 3\text{H}_2\text{O}$, and by the action of concentrated sulphuric acid it loses sulphur dioxide and yields an oil. This salt may also be obtained directly from the salt $\text{C}_{13}\text{H}_{21}\text{O}\cdot\text{SO}_3\text{Na}\cdot 1\frac{1}{2}\text{H}_2\text{O}$ by the action of sulphuric acid, by boiling the alcoholic solution with ethyl bromide, or by heating the alcoholic solution with a drop of concentrated sulphuric acid. The *semicarbazone*,



crystallises from ethyl acetate in white needles. Attempts to prepare the oxime and hydrazone failed. The *potassium salt*, $\text{C}_{13}\text{H}_{21}\text{O}\cdot\text{SO}_3\text{K}\cdot 3\text{H}_2\text{O}$, crystallises in white leaflets.

β -Ionone sodium hydrogen sulphite, $\text{C}_{13}\text{H}_{21}\text{O}\cdot\text{SO}_3\text{Na}\cdot 2\text{H}_2\text{O}$, prepared by dissolving β -ionone in a boiling solution of sodium hydrogen sulphite, is more soluble in cold than in hot water and separates from its solution on the addition of sodium chloride as an oil which has a sp. gr. 1.200 at 15° ; it crystallises from a concentrated aqueous solution and is readily soluble in ethyl acetate, acetone, or benzene. The *semicarbazone*, $\text{SO}_3\text{Na}\cdot\text{C}_{13}\text{H}_{21}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2\cdot 4\text{H}_2\text{O}$, forms small lustrous tablets and is soluble in warm water, but only sparingly so in ethyl acetate. The *oxime* separates as an oil on the addition of sodium chloride. The *calcium hydrogen sulphite compound* of β -ionone, $(\text{C}_{13}\text{H}_{21}\text{OSO}_3)_2\text{Ca}\cdot 4\text{H}_2\text{O}$, is much less soluble than the sodium compound, and when decomposed by sodium hydroxide gives a theoretical yield of β -ionone.

Chemically pure α - and β -ionones have been prepared from their sodium hydrogen sulphite compounds. The odour of the former is more delicate and penetrating than that of the ordinary preparation and somewhat resembles that of iris, whilst β -ionone has more the true violet odour. α -Ionone boils at 127.6° under 12 mm., at

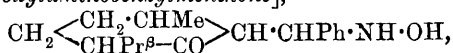
131.1° under 13, at 131.8° under 14, and at 134.3° under 16 mm. pressure; it has sp. gr. 0.9338 at 15°, 0.9301 at 20°, and n_D 1.50048 at 16.5° and 1.50001 at 17.2°. A kilogram of water dissolves 0.0935 parts of α -ionone. β -Ionone boils at 134.6° under 12 mm., at 136.8° under 13 mm., at 137.9° under 14 mm., and at 140.4° under 16 mm. pressure; it has sp. gr. 0.9488 at 15°, 0.9442 at 20°, and n_D 1.52070 at 16.8° and 1.52008 at 17.5°.

When β -ionone is boiled with a solution of *p*-bromophenylhydrazine in glacial acetic acid for an hour, the ordinary *p*-bromophenylhydrazone melting at 116° is not formed, but an isomeride which melts at 166–167° (compare Tiemann, Abstr., 1895, i, 530). Since the melting point of α -ionone-*p*-bromophenylhydrazone is not altered by treatment in this way, the reaction may be used to detect the presence of β -ionone. By boiling β -iononephenylhydrazone with glacial acetic acid, a compound which crystallises from methyl alcohol and melts at 121° is obtained.

α -Iononesemithiocarbazone, $C_{13}H_{20} \cdot N \cdot NH \cdot CS \cdot NH_2$, melts at 121° and is readily soluble in benzene; by the action of phthalic acid and steam, α -ionone is slowly regenerated. β -Iononesemithiocarbazone crystallises from dilute alcohol, melts at 158°, is readily soluble in benzene or alcohol, and is quickly decomposed by phthalic acid. Ironesemithiocarbazone, after repeated crystallisation from benzene and light petroleum, melts at 181°. E. W. W.

Chemically Pure α - and β -Ionones. DE LAIRE & Co. (*Chem. Centr.*, 1904, i, 282; from *Rev. gén. Chim. pure appl.*, 6, 471–473).—The ionone patents are discussed in connection with Chuit's work (see preceding abstract). Chuit's method of separating α - and β -ionones is not better than Tiemann's. E. W. W.

Menthone, Camphorphone, and Pinophorone. FRIEDRICH W. SEMMLER (*Ber.*, 1904, 37, 234–241).—*Benzylidenementhonehydroxylamine* [α -Hydroxylaminobenzylmenthone],



crystallises from light petroleum in needles melting at 162°, which, on reduction with sodium and alcohol, is converted into α -aminobenzylmenthol, $CH_2 \begin{array}{c} \text{CH}_2 - CHMe \\ \text{CHPr}^\beta \cdot CH(OH) \end{array} > CH \cdot CHPh \cdot NH_2$, an oil boiling at 202–206° under 15 mm. pressure, has a sp. gr. 1.013 at 20°, and n_D 1.5255.

Benzylmenthol is an oil boiling at 179–180° under 9 mm. pressure, which has a sp. gr. 0.9904 at 20° and n_D 1.5255, forming, on oxidation with chromic acid in acetic acid solution, *benzylmenthone*, $C_{17}H_{24}O$, an oil boiling at 175–180° under 10 mm. pressure, which has a sp. gr. 0.981 at 20°, n_D 1.515, and does not form an oxime.

Dihydrocamphoryl alcohol, $CHPr^\beta \begin{array}{c} < CH(OH) \\ CH_2 \cdot CH_2 \end{array} > CHMe$, obtained on reducing camphorphone, boils at 185–192°, has a sp. gr. 0.899 at 20°, n_D 1.4604, and has the odour of menthol. The *phenylurethane* crystallises in needles from methyl alcohol melting at 82°, the *acetate* boils at 92–94° under 14 mm. pressure, has a sp. gr. 0.930, and n_D

1.432. When heated with oxalic acid, an unsaturated hydrocarbon, "*anhydrocamphoryl alcohol*," [1-methyl-3-isopropyl- Δ^1 -cyclopentene] $\text{CHPr}^\beta \langle \begin{smallmatrix} \text{CH} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \rangle \text{CMe}$, is obtained, which boils at about $144\text{--}146^\circ$, has a sp. gr. 0.801 at 20° , and n_D 1.4478 ; it unites with two atoms of bromine.

Dihydrocamphorone, $\text{CHPr}^\beta \langle \begin{smallmatrix} \text{CO} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \rangle \text{CHMe}$, formed by the oxidation of the preceding alcohol with chromic acid, is an oil which boils at $184\text{--}185^\circ$, has a sp. gr. 0.887 , and n_D 1.4389 ; the *semicarbazone* melts at $196\text{--}197^\circ$ and the *oxime* at 79° . On oxidation with permanganate, two ketonic acids are formed and can be separated by means of their semicarbazones. One acid boils at $166\text{--}168^\circ$ under 14 mm. pressure, has a sp. gr. 1.0214 , n_D 1.4488 , and forms a *semicarbazone* melting at $167\text{--}168^\circ$ and an *oxime* melting at 75° ; as on further oxidation, α -methylglutaric acid is formed, it must have the formula $\text{COPr}^\beta \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$.

The other ketonic acid, which boils at 156° under 14 mm. pressure and forms a *semicarbazone* melting at 140° , has the formula $\text{CO}_2\text{H} \cdot \text{CHPr}^\beta \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe}$, since it is easily converted into *α -isopropylglutaric acid*.

Pinophorone, $\text{CH}_2 \cdot \text{CMeCH} \langle \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \rangle \text{CO}$, is produced, together with acetone and a hydrocarbon, C_9H_{14} , on distilling the calcium salt of pinonic acid. It boils at $203\text{--}205^\circ$, has a sp. gr. 0.9284 , n_D 1.4805 , and forms a *semicarbazone* melting at $157\text{--}158^\circ$, and with hydroxylamine an *oxime* which was not isolated, as in contact with mineral acids it is converted into a *piperidone*, $\text{C}_9\text{H}_{15}\text{ON}$, which boils at $136\text{--}140^\circ$ under 14 mm. pressure, has a sp. gr. 0.9904 and n_D 1.5014 , whilst on reduction with sodium and alcohol *pinocamphoryl alcohol*, $\text{C}_9\text{H}_{16}\text{O}$, is obtained; this boils at 203° , has a sp. gr. 0.921 at 20° , and n_D 1.483 .

The *hydrocarbon*, C_9H_{14} , obtained at the same time as pinophorone, boils at 140° , has a sp. gr. 0.8142 at 20° , and n_D 1.4628 . E. F. A.

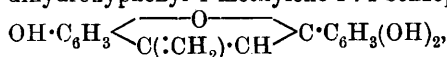
[Interaction of Mercuric Acetate with Terpenes and Compounds containing the C_5H_5 Group.] A Correction. LUIGI BALBIANO and VINCENZO PAOLINI (*Ber.*, 1904, 37, 225).—The compound previously described by the authors (this vol., i, 73) as hydroxyapiole is apiol, and that described as the benzoyl derivative of hydroxyapiole is a mixture of apiole and benzoic anhydride. A. MCK.

Phylloerythrin, a new Derivative of Chlorophyll. LÉON MARCHLEWSKI (*Bull. Acad. Sci. Cracow*, 1903, 638—642).—*Phylloerythrin*, obtained by extracting with cold chloroform the fresh excrement of a cow, fed entirely on grass, separates from this solvent in crystals, which are brownish-red with a tinge of violet when seen in mass. Solutions of phylloerythrin in acetic acid or chloroform give absorption spectra showing four bands, but the spectrum of the former solution is considerably modified by the addition of hydrochloric acid. Sulphuric acid dissolves phylloerythrin, forming a grass-green solution, the spectrum of which shows several bands, which are ill-defined with the exception of one in the red. In several respects, phylloerythrin

resembles scatocyanin (Schunk, Abstr., 1902, i, 301), but is distinguished by the absorption spectra of its solutions, illustrations of which are given in the original. T. A. H.

Composition of Furfuraldehyde-phloroglucide. W. GOODWIN and BERNHARD TOLLENS (*Ber.*, 1904, 37, 315—319).—Furfuraldehyde-phloroglucide probably has the composition $C_{11}H_8O_4$, but prolonged drying in the air results in a small increase in weight and a considerable decrease in the percentage of carbon (calc. 64·7, found, 63·9, 62·8, 61·9), probably owing to oxidation with liberation of carbon dioxide; a sample dried during $2\frac{1}{2}$ hours in a current of hydrogen gave carbon 65·1 per cent., and after $3\frac{1}{2}$ hours 64·5 per cent. T. M. L.

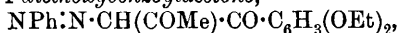
Synthesis of Nencki and Sieber's "Resacetein." CARL BÜLOW and CONST. SAUTERMEISTER (*Ber.*, 1903, 37, 354—368. Compare Abstr., 1881, 811, and 1903, i, 357).—Resacetein, $C_{16}H_{12}O_4$, or 7-hydroxy-2-op-dihydroxyphenyl-4-methylene-1:4-benzopyranol,



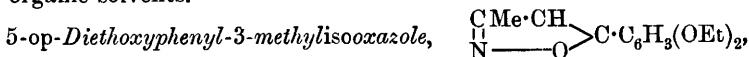
can be synthesised by condensing 2:4-diethoxybenzoylacetone with resorcinol and subsequently hydrolysing the ethoxy-groups in the condensation product.

2:4-Diacetoxybenzoylacetone forms a *copper* salt crystallising in greyish-green plates melting at 171° , which, when hydrolysed with dilute sulphuric acid, is converted into diethoxybenzoylacetone.

Benzeneazo-2:4-diethoxybenzoylacetone,

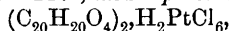


crystallises in glistening needles melting at $82-83^\circ$ and easily soluble in organic solvents.



crystallises from alcohol in long, silk, glistening needles melting at 126.5° .

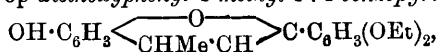
The *hydrochloride of resacetein diethyl ether* is formed on condensing diethoxybenzoylacetone and resorcinol in presence of hydrogen chloride; on heating, it blackens at $205-210^\circ$ and melts and decomposes at 235° . The free base crystallises in glistening, red needles which melt between 77° and 81° and form a *picrate* separating in dark golden-yellow needles melting and decomposing at 235° , a *sulphate* ($+2H_2O$) melting at $215-217^\circ$, and a *platinichloride*,



which separates in microscopic, orange-yellow needles.

8-Nitroso-7-hydroxy-2-op-dihydroxyphenyl-4-methylene-1:4-benzopyranol forms microscopic crystals with a bronze-like lustre melting between 170° and 178° , dissolves in sulphuric acid with a bluish-violet, and in alkali with a dark red coloration. 7-Acetoxy-2-op-dihydroxyphenyl-4-methylene-1:4-benzopyranol crystallises in glistening, red, hexagonal plates, dissolves in sulphuric acid forming a dark yellow solution which has a green fluorescence, and melts to a gummy mass between 228° and 242° .

7-Hydroxy-2-op-dihydroxyphenyl-4-methyl-1:4-benzopyran,

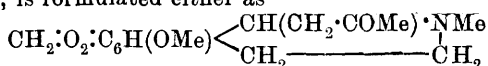


formed on reducing the free base with zinc dust and acetic acid, is a colourless, amorphous substance which, on heating, darkens at 118° and melts between 125° and 147° . The 7-acetoxy-derivative, which has marked electrical properties, sinters at about 100° and melts at 118° to a gummy mass.

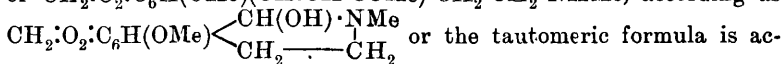
Resacetin, in every way identical with Nencki and Sieber's compound (*loc. cit.*), is best prepared from the diethoxyphenylmethylenbenzopyranol by heating it in sealed tubes with hydrochloric acid between 150° and 180° . The synthetical product forms a triacetate, $C_{22}H_{18}O_7$, identical with that described by Rasinsky (Abstr., 1882, 1288). When slowly distilled with aqueous sodium hydroxide, diethoxyphenylmethylenbenzopyranol is resolved into resorcinol and resacetophenone diethyl ether. E. F. A.

Condensations of Cotarnine and Hydrastinine with Ketones.

CARL LIEBERMANN and F. KROPF (*Ber.*, 1904, 37, 211—216).—*Anhydrocotarnineacetone*, prepared by the condensation of cotarnine with acetone, is formulated either as



or $CH_2:O_2:C_6H(OMe)(CH:CH \cdot COMe) \cdot CH_2 \cdot CH_2 \cdot NHMe$, according as



Anhydrohydrastinineacetone, $CH_2:O_2:C_6H_2 \begin{array}{c} \text{CH}(CH_2 \cdot COMe) \cdot NMe \\ \text{CH}_2 \text{-----} \text{CH}_2 \end{array}$ or $CH_2:O_2:C_6H_2(CH:CH \cdot COMe) \cdot CH_2 \cdot CH_2 \cdot NHMe$, prepared from hydrastinine and acetone, melts at 72° . Its *platinichloride* melts at 196 — 198° .

Anhydrocotarninemethyl propyl ketone, $C_{17}H_{23}O_4N$, prepared from cotarnine and methyl propyl ketone, melts at 86 — 92° . *Anhydrocotarnine-acetophenone*, $C_{20}H_{21}O_4N$, prepared from cotarnine and acetophenone, separates from alcohol in colourless prisms and melts at 126° . *Anhydrohydrastinine-acetophenone*, $C_{19}H_{19}O_3N$, crystallises in prisms and melts at 74° . A. McK.

Cytisine. MARTIN FREUND (*Ber.*, 1904, 37, 16—23. Compare Abstr., 1901, i, 288).—Cytisoline, $C_{11}H_{11}ON$, the chief product of the reduction of cytisine with phosphorus and hydriodic acid, melts at 199° and not at 192° as previously stated. It is oxidised by chromic acid to *cystolinic acid*, $C_{11}H_9O_3N$, which crystallises from acetic acid in minute needles, the melting point of which lies above 350° ; it has acid properties, dissolves readily in ammonia, and is precipitated by acids. Nitric acid gives a *nitrocytisoline*, $C_{11}H_{10}O_3N_2$, which separates from alcohol in yellow crystals, sinters at 240° , and melts at 275° . Reduction with sodium in alcohol converts cytisolin into *α-cytisolidine*,

$C_{11}H_{15}N$, a coniine-like base which forms a *platinichloride* melting at 216° and a picrate melting at $228-229^\circ$.

An isomeride of cytisolidine to which the name of *β -cytisolidine* is given is produced as a by-product in the preparation of cytisoline; the *platinichloride* crystallises from alcohol and hydrochloric acid and melts at 207° ; the *hydrochloride* forms small, silky needles and melts at $250-260^\circ$; the *picrate* crystallises from alcohol in needles and sinters at $225-228^\circ$.

T. M. L.

Epinephrine and its Degradation Products. JOHN J. ABEL (*Ber.*, 1904, 37, 368-381. Compare *Abstr.*, 1899, i, 395; 1903, i, 278; also Jowett, *Trans.*, 1904, 85, 192).—When oxidised with nitric acid, epinephrine yields oxalic acid and a substance containing nitrogen, which forms a yellow, crystalline, hygroscopic derivative with iodine trichloride and an *aurichloride*, $C_3H_4ON_2 \cdot HAuCl_4$, crystallising in prisms. The nitrogen compound, $C_3H_4ON_2$, is held to be a pyrazolone derivative; alkalis react with it forming methylamine. Analytical evidence is adduced in favour of the formula $C_{10}H_{13}O_3N \cdot \frac{1}{2}H_2O$ for epinephrine, and the results obtained by previous workers are discussed.

E. F. A.

Synthesis of Ethyl 2:5-Dimethylpyrrole-3-monocarboxylate. IWAN P. OSSIPOFF and G. KORSCHUN (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 630-635).—Ethyl 2:5-dimethylpyrrole-3-carboxylate may be obtained by the action of aqueous ammonia on ethyl 2:5-hexadione-3-carboxylate (ethyl $\alpha\beta$ -diacetylpropionate), or, in better yield, by using alcoholic ammonia under a high pressure (150°). It forms rhombic crystals (see Knorr, *Abstr.*, 1885, 994).

T. H. P.

Synthesis of Trialkylpyrrolemonocarboxylic Compounds. G. KORSCHUN (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 635-636).—Ethyl 1:2:5-trimethylpyrrole-3-carboxylate, prepared by the action of methylamine on ethyl diacetylpropionate in the cold, is soluble in alcohol, benzene, and other organic solvents, and separates from aqueous alcohol in long, acicular crystals, melts at 48° , and is volatile in a current of steam. The corresponding *acid* decomposes, without melting, at about 175° .

Ethyl 2:5-dimethyl-1-ethylpyrrole-3-carboxylate is a viscid, yellow liquid, which has a sp. gr. 1.0122 at $24/15^\circ$, boils at 286° (uncorr.) under 748 mm. pressure, and exhibits normal cryoscopic behaviour in benzene. The corresponding *acid*, when heated, does not melt, but decomposes, yielding 2:5-dimethyl-1-ethylpyrrole.

2:5-Dimethyl-1-butylpyrrole-3-carboxylic acid, obtained by hydrolysing the product of the action of normal butylamine on ethyl diacetylpropionate, forms a white, crystalline mass which melts at 154° , dissolves in alcohol, and, to a less extent, in benzene, and in the latter shows normal cryoscopic behaviour.

T. H. P.

Synthesis of Ethyl 1:2:5-Trimethylpyrrole-3-carboxylate. G. KORSCHUN and TREFILIEFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 636).—This compound (see preceding abstract) may be obtained free

from ethyl 2:4:5-trimethylpyrrole-3-carboxylate by the action of methyl iodide on potassium 2:5-dimethylpyrrole-3-carboxylate.

T. H. P.

Derivatives of 2-Picolyl- and 2-Picolylmethyl-alkine. I. KARL LÖFFLER (*Ber.*, 1904, 37, 161—174).—2-Picolylalkine [2- β -hydroxyethylpyridine] (Ladenburg, *Abstr.*, 1898, i, 687) reacts with fuming hydriodic acid and red phosphorus (compare Koenigs and Hoppe, *Abstr.*, 1902, i, 394) when heated in a sealed tube at 120—130°, forming an iodide, $C_5H_4N \cdot CH_2 \cdot CH_2I$, a volatile oil giving an irritating vapour and dissolving sparingly in water, readily in alcohol or ether. The *picrate*, $C_7H_8NI \cdot C_6H_3O_7N_3$, crystallises from benzene in short, highly refractive prisms and melts at 111—112°. The *platinichloride*, $(C_7H_8NI)_2 \cdot H_2PtCl_6$, is a dark red, crystalline precipitate melting and decomposing at 149—150°.

Heating converts the iodo-base into a solid isomeride having the constitution of a pyridinium iodide, $\begin{array}{c} CH \cdot CH \cdot C - CH_2 \\ | \\ CH \cdot CH \cdot NI \cdot CH_3 \end{array}$, crystallising from water in slightly yellow needles and melting at 211—213°.

Hydrobromic acid and red phosphorus convert 2- β -hydroxyethylpyridine into a *bromide*, $C_5NH_4 \cdot C_2H_4Br$, which may be isolated as a volatile, colourless oil by distillation with steam. The *platinichloride*, $(C_7H_8NBr)_2 \cdot H_2PtCl_6$, is a flesh-coloured, amorphous precipitate melting at 171—172°; the *picrate* crystallises from benzene in yellow rosettes and melts at 95—96°. The base passes gradually into the isomeric pyridinium bromide, which forms long needles containing $1H_2O$; the dried salt melts at 226—227° and dissolves readily in cold water, very sparingly in alcohol. Moist silver oxide precipitates silver bromide; the filtrate is alkaline and red in colour. Potassium iodide precipitates the crystalline iodide from a solution of the bromide. Moist silver chloride forms the chloride, crystallising from alcohol in prisms containing H_2O , and melting, when dry, at 175°. The *platinichloride*, $(C_7H_8NCl)_2 \cdot PtCl_4$, is an amorphous powder.

Alkylamines react at 100° with the volatile bromo-base to form alkylaminoethylpyridines. Diethylamine forms 2- β -diethylaminoethylpyridine, $C_5H_4N \cdot C_2H_4 \cdot NEt_2$, a colourless liquid boiling at 115—116° under 13 mm. pressure and having an odour of nicotine. The *hydrochloride* is a white, deliquescent powder melting at 172—173°; the *platinichloride*, $C_{11}H_{18}N_2 \cdot H_2PtCl_6$, forms thin, golden leaflets and melts and decomposes at 226°; the *aurichloride* forms small, yellow crystals and melts at 184°. The *normal picrate* melts at 163—164° and the readily soluble *basic picrate* at 96—97°. The *mercurichloride* crystallises in needles and melts at 103—104°.

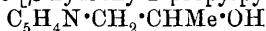
2- β -Methylaminoethylpyridine, $C_5H_4N \cdot C_2H_4 \cdot NHMe$, from methylamine, is a colourless base boiling at 113—114° under 30 mm. pressure. The *platinichloride*, $C_8H_{12}N_2 \cdot H_2PtCl_6 \cdot 2H_2O$, forms very large, orange needles; the *aurichloride*, small, yellow needles, melts and decomposes at 205°; the *normal picrate*, glistening needles, melts at 193—194°, and the *basic picrate*, hexagonal prisms, at 137—138°.

Alcoholic ammonia at 125° converts the bromo-base into 2- β -amino-

ethylpyridine, $C_5H_4N \cdot C_2H_4 \cdot NH_2$, boiling at $92-93^\circ$ under 12 mm. pressure, colouring litmus blue, and fuming with hydrochloric acid. The *hydrobromide* crystallises from alcohol in glistening, almost colourless leaflets and melting at 129° . The *platinichloride* separates from water in long needles containing $2H_2O$, and melts and decomposes at $232-233^\circ$. The *picrate* forms long, slender needles and melts at $215-216^\circ$. 2- β -Acetylaminooethylpyridine, $C_5H_4N \cdot C_2H_4 \cdot NHAc$, is a viscid oil boiling at 175° . Attempts to produce condensation to an isoquinoline derivative were unsuccessful.

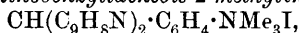
Together with the primary base, a secondary base, $(C_5H_4N \cdot C_2H_4)_2NH$, is obtained, boiling at 192° under 8 mm. pressure and possessing strongly marked basic properties. The *hydrochloride* crystallises from alcohol in small needles, the *platinichloride*, $(C_{14}H_{17}N_3)_2 \cdot 3H_2PtCl_6 \cdot 2H_2O$, forms small, orange needles; the *picrate*, long, yellow needles, melts at $181-183^\circ$, and the *mercurichloride*, glistening leaflets, at $121-122^\circ$. Nitrous acid forms a nitroso-derivative, $(C_5H_4N \cdot C_2H_4)_2N \cdot NO$, a slightly red oil. The *platinichloride* forms orange needles.

2-Picolylmethylalkine [β -hydroxy-2-propylpyridine],

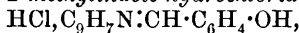


(Ladenburg, *loc. cit.*), also reacts with hydriodic acid, forming the iodo-base, a volatile oil, passing slowly into a crystalline isomeride. The *platinichloride*, $(C_8H_{10}NI)_2 \cdot H_2PtCl_6$, forms groups of reddish-brown needles and melts and decomposes at $152-153^\circ$. C. H. D.

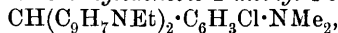
Indole Dyes. MARTIN FREUND [with GUSTAV LEBACH] (*Ber.*, 1904, 37, 322-323. Compare Abstr., 1903, i, 278).—The following substances have been obtained by condensing 2-methylindole with aldehydes. *p*-Dimethylaminobenzylidenebis-2-methylindole methiodide,



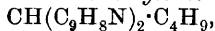
white needles melting at $181-182^\circ$. *o*-Hydroxybenzylidenebis-2-methylindole, $CH(C_9H_8N)_2 \cdot C_6H_4 \cdot OH$, white needles melting at $230-231^\circ$. *o*-Hydroxybenzylidene-2-methylindole hydrochloride,



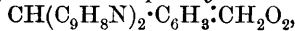
red flakes melting at 202° . *o*-Nitrobenzylidenebis-2-methyl-1-ethylindole, $CH(C_9H_7NEt)_2 \cdot C_6H_4 \cdot NO_2$, white needles melting at 229° . *o*-Chloro-*p*-dimethylaminobenzylidenebis-2-methyl-1-ethylindole,



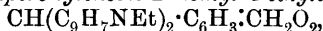
white needles melting at 219° . *Valerylenebis-2-methylindole*,



white needles melting at 157° . *Piperonylenebis-2-methylindole*,



white needles melting at 213° . *Piperonylene-2-methylindolehydrochloride*, $HCl, C_9H_7N : CH \cdot C_6H_3 \cdot CH_2O_2$, reddish-brown, glistening scales melting at 194° . *Piperonylenebis-2-methyl-1-ethylindole*,



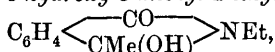
white needles melting at 175° .

T. M. L.

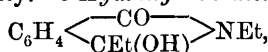
Action of Organomagnesium Compounds on Alkylated Phthalimides. FRANZ SACHS and AL. LUDWIG (*Ber.*, 1904, 37, 385-390).—Magnesium does not react with ω -bromoalkylphthalimides, and the synthesis of amino-alcohols by this means is therefore

impossible. Magnesium alkyl haloids, however, react with alkylphthalimides, and the results obtained are in accordance with those obtained by Béis (this vol., i, 15) and Bouveault (this vol., i, 13).

Magnesium methyl bromide reacts with ethylphthalimide at low temperatures, forming 3-hydroxy-3-methyl-2-ethylisoindolinone,



which crystallises from water below 70° in leaflets, and melts and decomposes at 93—94°, dissolving readily in most solvents and separating with difficulty. 3-Hydroxy-2:3-diethylisoindolinone,



from magnesium ethyl bromide, forms rhombic crystals and melts at 129—130°. Ethylphthalimide and magnesium phenyl bromide form 3-hydroxy-3-phenyl-2-ethylisoindolinone, which crystallises from dilute acetone or alcohol in prismatic needles and melts at 166—167°. Hydrochloric acid at temperatures not higher than 120° forms the hydrochloride, crystallising from water in hexagonal prisms and melting at 189°. Further heating with hydrochloric acid at 160—170° causes hydrolysis, with the formation of *o*-benzoylbenzoic acid.

The reaction takes place differently in the case of benzoisulphinide which is otherwise closely related to phthalimide. Ethylbenzoisulphinide and magnesium ethyl bromide form a compound, $\text{C}_{13}\text{H}_{21}\text{O}_3\text{NS}$, probably $\text{OH}\cdot\text{Cet}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NHEt}$, crystallising from ether in large, acute rhombohedra and melting at 99—100°. The compound from ethylbenzoisulphinide and magnesium phenyl bromide, $\text{C}_{21}\text{H}_{21}\text{O}_3\text{NS}$, crystallises from alcohol and melts at 184—185°, dissolving in concentrated sulphuric acid to an intense yellowish-red solution, in accordance with its representation as a derivative of triphenylcarbinol.

C. H. D.

1:8-Dimethyltetrahydroquinoline. MARTIN FREUND (*Ber.*, 1904, 37, 22—23).—This compound was synthesised because it appeared probable that it might be identical with cytisolidine (see this vol., i, 263).

1:8-Dimethyltetrahydroquinoline, $\text{C}_9\text{NH}_9\text{Me}_2$, boils at 238—240° (uncorr.); the *platinichloride* forms small, stout, yellow needles and decomposes at 223°; the *picrate* crystallises from 96 per cent. alcohol in small, yellowish-red, rhombic tablets and melts at 160°.

T. M. L.

Benzidine Isomerism. MICHAEL M. TICHWINSKY (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 667—675).—In the action of hydrochloric acid on hydrazobenzene, yielding benzidine and isobenzidine, the author considers that the strong mineral acid, in aqueous or alcoholic solution, tends to the formation of a stronger base, that is, to the transformation of tervalent into quinquevalent nitrogen. In cases where the hydrogen chloride does not exhibit its acid properties, owing to non-ionisation, as, for example, in benzene solution, such a transformation does not take place.

The author's experiments show that when azobenzene in acetic acid

solution is saturated with hydrogen bromide, it yields benzidine, 2:4-dibromoaniline, and *p*- and *o*-bromoaniline; a similar reaction occurs with hydrogen chloride, but hydrogen iodide undergoes oxidation with liberation of iodine.

These results point to the quinonoid structure of azobenzene, so that nearly all pigments can be referred to the quinone type.

T. H. P.

Interaction of Zinc Ethyl and Benzenediazonium Chloride. II. Ethylation of Benzidine. MICHAEL M. TICHWINSKY (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 675—678. Compare Abstr., 1903, i, 441).—In the author's previous paper (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 155; *loc. cit.*), he gave the melting point 116° to *s*-diethylbenzidine, whilst Hofmann (*Annalen*, 1860, 115, 365) described under this name a compound melting at 65° . The author has now prepared the latter compound, which he finds to consist of a mixture of about 85 per cent. of *s*-diethylbenzidine with 15 per cent. of tetraethylbenzidine, which melts at 90° .

T. H. P.

Degradation of Dihydroxytetramethylrosaminesulphonic Acid. CARL LIEBERMANN and A. GLAWE (*Ber.*, 1904, 37, 203—210. Compare Liebermann, Abstr., 1903, i, 860).—When dihydroxytetramethylrosaminesulphonic acid, $\text{NMe}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{C}(\text{OH})_2 \cdot \text{C}_6\text{H}_3 \cdot \text{NMe}_2 \cdot \text{SO}_2$, is boiled with aqueous potassium hydroxide for 1—2 hours, the resulting oil is a mixture of tetramethyldiaminoxanthone, $\text{NMe}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CO}$, and tetramethyldiaminoxanthen, $\text{NMe}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH}_2$, which may be separated by glacial acetic acid.

Tetramethyldiaminoxanthone crystallises in needles and melts at 240° , whilst tetramethyldiaminoxanthen also forms needles and melts at 113° . The identity of those compounds with the substances prepared by Biehringer from formaldehyde and dimethylaminophenol (Abstr., 1897, i, 73) is established. The platinichlorides of tetramethyldiaminoxanthone and tetramethyldiaminoxanthen also resemble the corresponding compounds prepared by Biehringer.

The presence of tetramethyldiaminoxanthen along with tetramethyldiaminoxanthone and catecholsulphonic acid as products of the hydrolysis of dihydroxytetramethylrosaminesulphonic acid is shown to be due to the presence in the dihydroxytetramethylrosaminesulphonic acid used of a small amount of its leuco-derivative.

The fact that the degradation of dihydroxytetramethylrosaminesulphonic acid can be effected with so much greater ease than the corresponding change with rosaniline and methyl-violet, malachite-green, &c., is due to the acidic hydroxyl and sulphonic groupings.

The degradation of tetramethylrosaminesulphonic acid proceeds in an analogous manner; potassium dimethylaminohydroxybenzophenonemonosulphonate, prepared by heating an aqueous solution of tetramethylrosaminesulphonic acid with potassium hydroxide, separates in pink leaflets.

A. McK.

Diphenyleneazone Series. FRITZ ULLMANN and PAUL DIETERLE (*Ber.*, 1904, 37, 23—36).—Diphenyleneazone oxide, $\text{C}_6\text{H}_4 \cdot \text{N} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{C}_6\text{H}_4 \cdot \text{N} > \text{O}$, prepared by reducing 2:2'-dinitrodiphenyl with sodium sulphide, melts at 139° and not at 152° as stated by Täuber (*Abstr.*, 1892, 183). The diphenazone, $\text{C}_6\text{H}_4 \cdot \text{N} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{C}_6\text{H}_4 \cdot \text{N}$, prepared by reducing with stannous chloride, is purer than that produced by the old method and melts at 156°; the *zincchloride* of the methochloride forms yellow needles, is readily soluble in water and sparingly so in alcohol, and melts at 235°.

3:8-Dimethyldiphenyleneazone oxide, $\text{C}_6\text{H}_3\text{Me} \cdot \text{N} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{C}_6\text{H}_3\text{Me} \cdot \text{N} > \text{O}$, prepared from 2:2'-dinitro-4:4'-ditolyl, crystallises from benzene in large, clear plates and melts at 209°. 3:8-Dimethyldiphenyleneazone, $\text{C}_6\text{H}_3\text{Me} \cdot \text{N} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{C}_6\text{H}_3\text{Me} \cdot \text{N}$, prepared by the electrolytic reduction of the dinitroditolyl, crystallises from benzene in sulphur-yellow crystals, melts at 188°, and is identical with the compound described by L. Meyer (*Abstr.*, 1893, i, 733); the *nitrate* separates from dilute nitric acid in yellow needles and melts at 166°; the *zincchloride* of the methochloride, $(\text{C}_{14}\text{H}_{12}\text{N}_2\text{MeCl})_2 \cdot \text{ZnCl}_2$, crystallises in small, yellow needles, melts at 231°, and is readily soluble in water.

3:8-Diaminodiphenyleneazone, $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{N} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{C}_6\text{H}_3 \cdot \text{N} \cdot \text{NH}_2$, prepared by the electrolytic reduction of dinitrobenzidine, crystallises from boiling xylene in stout, dark green crystals, melts at 265°, and is identical with the substance prepared by Täuber (*Abstr.*, 1892, 184).

4:4'-Tetramethyldiaminodiphenyl, $\text{C}_{12}\text{H}_8(\text{NMe})_2$, prepared by oxidising dimethylaniline with sulphuric acid and turpentine, crystallises from benzene in colourless flakes and melts at 197°. The 2:2'-dinitro-derivative crystallises from xylene or acetic acid in garnet-red needles, melts at 229·5°, decomposes at a slightly higher temperature, and is not identical with the substance described by Michler and Pattinson (*Abstr.*, 1884, 747). 3:8-Tetramethyldiaminodiphenyleneazone oxide, $\text{NMe}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{N} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{C}_6\text{H}_3 \cdot \text{N} \cdot \text{NMe}_2 > \text{O}$, crystallises from alcohol in radiating groups of carmine-red needles and melts at 242°. 3:8-Tetramethyldiaminodiphenyleneazone, $\text{NMe}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{N} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{C}_6\text{H}_3 \cdot \text{N} \cdot \text{NMe}_2$, crystallises from xylene in silky, red needles and melts at 270°. The *hydrochloride*, $\text{C}_{16}\text{H}_{18}\text{N}_4 \cdot \text{HCl}$, separates from hydrochloric acid in bluish-black crystals, melts at 236°, and yields a blue solution in dilute hydrochloric acid. The *nitrate* is a dark blue crystalline powder and melts at 238°.

2:2'-Diamino-4:4'-tetramethyldiaminodiphenyl, $\text{C}_{12}\text{H}_6(\text{NH}_2)_2(\text{NMe}_2)_2$, crystallises from a mixture of benzene and light petroleum in colourless flakes and melts at 166°.

4:4'-Tetraethyldiaminodiphenyl, $\text{C}_{12}\text{H}_8(\text{NEt}_2)_2$, prepared by oxidising diethylaniline with sulphuric acid and turpentine, is identical with

that prepared by other methods. The 2:2'-dinitro-derivative melts at 132° and not at 140° as described by Eppstein. 3:8-Tetraethyl-diaminodiphenyleneazone, $\text{NEt}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{N} \begin{array}{c} | \\ | \\ | \end{array} \text{N} \cdot \text{C}_6\text{H}_3 \cdot \text{N} \begin{array}{c} | \\ | \\ | \end{array} \text{NEt}_2$, forms glistening, dark crystals which become red when dried on the water-bath and melt at 184°.

6:6'-Dinitro-4:4'-diamino-3:3'-dimethoxydiphenyl

$\text{C}_{12}\text{H}_4(\text{OMe})_2(\text{NH}_2)_2(\text{NO}_2)_2$, crystallises from alcohol in red flakes, melts at 222°, and agrees with the properties of the substance described by Starke. 3:8-Diamino-2:9-dimethoxydiphenyleneazone, $\text{OMe} \cdot \text{C}_6\text{H}_2(\text{NH}_2) \cdot \text{N} \begin{array}{c} | \\ | \\ | \end{array} \text{N} \cdot \text{C}_6\text{H}_2(\text{NH}_2) \cdot \text{OMe}$, prepared by the electrolytic reduction of the nitro-compound, separates from alcohol in dark yellow crystals and melts at 244°. The hydrochloride, $\text{C}_{14}\text{H}_{14}\text{O}_2\text{N}_4 \cdot 2\text{HCl}$, separates in red crystals with a metallic lustre and begins to lose hydrogen chloride at 105°. T. M. L.

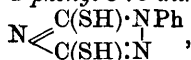
Reactions in the Urazole Series. SALOMON F. ACREE (*Amer. Chem. J.*, 1904, 31, 185—188. Compare Abstr., 1902, i, 242; 1903, i, 867).—A reply to Wheeler and Johnson (Abstr., 1903, i, 693).

E. G.

1-Phenyl-3:5-dithiolurazole. SALOMON F. ACREE and O. W. WILLCOX (*Ber.*, 1904, 37, 184—185. Compare Abstr., 1902, i, 242; 1903, i, 867).—Ethyl phenylthiosemicarbazidecarbothionoxylate,



obtained by heating ethyl chlorothiocarbonate (Klason, Abstr., 1887, 1029) with phenylthiosemicarbazide in acetone solution, crystallises from alcohol and melts and decomposes at 173°. When boiled for several hours with sodium hydroxide solution and then acidified with hydrochloric acid, it yields 1-phenyl-3:5-dithiolurazole,



melting at 181°. When titrated with alkali, using phenolphthalein as indicator, this behaves as a monobasic acid, and also yields only a mono-silver salt. J. J. S.

Carbazoles. E. DELÈTRA and FRITZ ULLMANN (*Arch. Sci. phys. nat.*, 1904, [v], 17, 78—92. Compare Graebe and Ullmann, Abstr., 1896, i, 575, and Ullmann, Abstr., 1898, i, 591).—3:4-o-Tolylazimino-

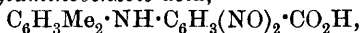
benzoic acid, $\text{N} \begin{array}{c} \diagup \text{N}(\text{C}_6\text{H}_4\text{Me}) \\ \diagdown \end{array} \text{C}_6\text{H}_3 \cdot \text{CO}_2\text{H}$, prepared by diazotising 3-amino-4-o-tolylaminobenzoic acid (Heidensleben, Abstr., 1891, 306), forms small, acicular crystals, melts at 204°, and is very soluble in alcohol and benzene, less so in ether, and insoluble in boiling water. When heated with twice its weight of lime, it is converted into

1-methylcarbazole, $\text{NH} \begin{array}{c} \diagup \text{C}_6\text{H}_3\text{Me} \\ \diagdown \text{C}_6\text{H}_4 \end{array}$ This forms white, tabular crystals,

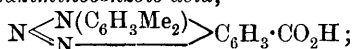
melts at 120°, gives a green colour with sulphuric acid, and is soluble in alcohol or ether, less so in acetic acid, and insoluble in water; the *picrate* forms red needles and melts at 143°.

2-Nitro-4-*p*-tolylaminobenzoic acid, prepared by condensing 4-chloro-3-nitrobenzoic acid with *p*-toluidine (compare Schöpf, Abstr., 1890, 374), on reduction with aluminium and sodium hydroxide furnishes the corresponding *amino*-compound, which crystallises in transparent, lanceolate needles, melts at 183°, and is insoluble in acetic acid and alcohol, less so in ether and benzene. Its solution in ether exhibits a violet fluorescence. On diazotisation, it furnishes 3:4-*p*-tolylazimino-benzoic acid, which melts at 267°, is soluble in acetic acid, alcohol, and benzene, less so in ether and light petroleum, and, when distilled with lime, furnishes 3-methylcarbazole. This crystallises in white scales, melts at 203°, gives a fugitive green colour with sulphuric acid, which is intensified by the addition of nitric acid, and resembles 1-methylcarbazole in solubility. Its solutions in alcohol, ether, and benzene exhibit a violet fluorescence. The *picrate* forms bright red needles, melts at 180°, and is soluble in alcohol and benzene.

2-Nitro-4-*m*-xylylaminobenzoic acid,

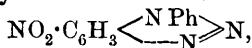


obtained by condensing *m*-xylidine with 4-chloro-3-nitrobenzoic acid, is a bright red, crystalline powder and melts at 213°. On reduction with aluminium powder, it furnishes the corresponding *amino*-acid, which crystallises in grey masses, melts at 179°, and when diazotised yields 3:4-*m*-xylylaziminobenzoic acid,



this crystallises from nitrobenzene in rose-tinted prisms, melts at 230°, and is soluble in alcohol and acetic acid. When distilled with lime, it furnishes *p*-methylacridine and 1:3-dimethylcarbazole. The latter is a white, crystalline powder which melts at 95°, gives a green coloration with sulphuric acid, and is very soluble in alcohol, acetone, and benzene, less so in acetic acid; the *picrate* forms red needles, melts at 188°, and is soluble in alcohol and benzene.

4-Nitro-2-aminodiphenylamine, prepared by reducing dinitrodiphenylamine with sodium sulphide, melts at 134° (compare Nietzki, Abstr., 1895, 164). Its hydrochloride, when diazotised in acetic acid solution, furnishes phenylazimino-4-nitrobenzene,



which melts at 168° (compare Nietzki, *loc. cit.*). This does not yield 3-nitrocarbazole on distillation, but on reduction with stannous chloride to phenylazimino-4-aminobenzene and distillation of the latter at 320–330° suspended in paraffin, 3-aminocarbazole, $\text{C}_{12}\text{NH}_8\cdot\text{NH}_2$, was obtained. This crystallises in colourless, transparent scales, melts at 254°, gives an azure-blue colour with sulphuric acid, which becomes purple on addition of nitric acid, and is soluble in alcohol and ether; the solutions in these solvents exhibit a violet fluorescence. The *picrate* forms transparent rosettes, becomes yellow and opaque at 100°, and melts and decomposes at about 220°. When diazotised and

condensed with β -naphthol, *p*-aminocarbazole furnishes a red dye of the formula $C_6H_4 \begin{smallmatrix} \text{NH} \\ | \\ C_6H_3 \cdot N:N \cdot C_{10}H_6 \cdot OH \end{smallmatrix}$. 3-Acetylaminocarbazole forms silvery scales, melts at 217° , and is soluble in alcohol and acetic acid, slightly so in ether and benzene.

2:4-Dinitrodiphenylethylamine, $C_6H_5(NO_2)_2 \cdot NEtPh$, obtained by condensing 1-chloro-2:4-dinitrobenzene with ethylaniline, forms fine, coral-red, lanceolate crystals, melts at 97.5° , and gives a red colour with sulphuric acid. It is very soluble in benzene, less so in alcohol and ether. When dissolved in alcohol and reduced by ammonium sulphide in presence of ammonia, it yields 4-nitro-2-aminodiphenylethylamine, $NO_2 \cdot C_6H_5(NH_2) \cdot NEtPh$, which forms dark red crystals, melts at 86.5° , gives a red colour with sulphuric acid, and is readily soluble in acetic acid and alcohol. The *sulphate* forms golden-brown plates and melts at 98° . The diazonium salt resulting from its diazotisation, when warmed in presence of metallic copper, furnishes 3-nitro-9-ethylcarbazole, a red, crystalline powder, which melts and decomposes at 108° , gives an intense reddish-violet colour with sulphuric acid, and is readily soluble in acetic acid and benzene, slightly so in alcohol and ether. It does not form a picrate.

T. A. H.

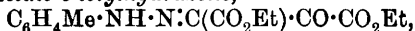
Curtius's 4-Bis-3-methylpyrazolone. CARL BÜLOW (*Ber.*, 1904, 37, 91—95).—Curtius's 4-bis-3-methylpyrazolone (*Abstr.*, 1894, i, 247) is in reality 3:6-dimethyldihydropyridazine-4:5-dicarboxylic acid cyclohydrazone, $\begin{smallmatrix} \text{NH} \cdot \text{CMe} \cdot \text{C} \cdot \text{CO} \cdot \text{NH} \\ | \\ \text{NH} \cdot \text{CMe} \cdot \text{C} \cdot \text{CO} \cdot \text{NH} \end{smallmatrix}$; this is shown by the ease with which

it loses hydrazine on boiling with dilute acids and by its being formed on boiling ethyl dimethylpyridazinedicarboxylate (Paal and Ueber, *Abstr.*, 1903, i, 290) with alcoholic hydrazine hydrate. It is soluble in both acids and alkalis; the *hydrochloride*, $C_8H_{10}O_2N_4 \cdot HCl \cdot H_2O$, forms thick, lustrous needles, and the *tetrabenzoyle* derivative, $C_{86}H_{26}O_6N_4$, prepared by the Schotten-Baumann method, crystallises from hot alcohol in small, broad needles and melts at 189 — 191° .

W. A. D.

Action of Diazochlorides on Oxalacetic Esters. JULIEN RABISCHONG (*Bull. Soc. chim.*, 1904, [iii], 31, 76—83. Compare Wislicenus and Jensen, *Abstr.*, 1893, i, 146; Favrel, *Abstr.*, 1901, i, 167, and succeeding abstract).— β -Ethyl oxalacetatephenylhydrazone, $NHPh \cdot N:C(CO_2Et) \cdot CO \cdot CO_2Et$, obtained by the action of diazobenzene chloride on ethyl oxalacetate in presence of sodium acetate (compare Wislicenus and Jensen, *loc. cit.*), forms yellowish-red crystals, melts at 72 — 73° , and is soluble in aqueous solutions of sodium hydroxide or carbonate; when treated with potassium ethoxide, dissolved in alcohol, it appears to form a *potassium* derivative. When the *sodium* derivative, similarly obtained, dissolved in alcohol, is treated with dilute hydrochloric acid, there is precipitated α -ethyl oxalacetatephenylhydrazone, which is crystalline and melts at 126 — 127° .

Methyl oxalacetatephenylhydrazone, similarly prepared, crystallises from xylene and melts at 104 — 105° .

β-Ethyl oxalacetate-o-tolylhydrazone,

separates from boiling alcohol in yellow crystals and melts at 86—87°. When its *sodium* derivative, dissolved in alcohol, is treated with dilute hydrochloric acid, the *α*-isomeride is precipitated in the course of several days; this crystallises from alcohol and melts at 155—156°. These hydrazones all give a violet coloration with sulphuric acid and potassium dichromate. No hydrazones were obtained by the interaction of oxalacetic esters with the chlorides of diazo-*p*-toluene and diazo-*m*-toluene.

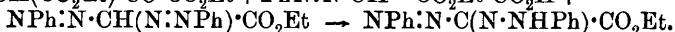
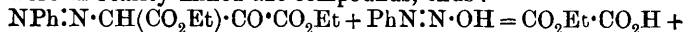
T. A. H.

Action of Diazochlorides on Oxalacetic Esters in presence of Alkalis. JULIEN RABISCHONG (*Bull. Soc. chim.*, 1904, [iii], 31, 83—86. Compare preceding abstract).—Ethyl diphenylformazylformate, $\text{NPh}\cdot\text{N}\cdot\text{C}(\text{N}\cdot\text{NHPh})\cdot\text{CO}_2\text{Et}$, obtained by the addition of excess of diazobenzene chloride to ethyl oxalacetate, dissolved in alcohol containing sodium hydroxide, melts at 116—117° (compare Bamberger and Wheelwright, *Abstr.*, 1893, i, 84; Wislicenus and Jensen, *ibid.*, 146) and dissolves in an aqueous solution of sodium hydroxide, forming a yellow liquid which becomes violet on addition of acids.

Ethyl o-ditolylformazylformate, similarly prepared, crystallises from anhydrous alcohol, melts at 99—100°, and behaves like its lower homologue with alkalis and acids.

T. A. H.

Action of Diazobenzene Chloride on Substituted Hydroxy-fumaric Esters. JULIEN RABISCHONG (*Bull. Soc. chim.*, 1904, [iii], 31, 91—96).—The author has regarded the first products of the action of diazobenzene chloride on oxalacetic esters as hydrazones, since by the further action of diazobenzene they are converted into formazyl derivatives (compare two preceding abstracts). It would, however, be possible to explain the formation of the latter if the first products were in reality mixed azo-compounds, thus:



This investigation has therefore been extended to substituted oxalacetic esters, the ethyl acetoxyfumarate and ethyl *α*-acetyl-*β*-hydroxyfumarate simultaneously produced when ethyl sodio-oxalacetate is treated with acetyl chloride (Nef, *Abstr.*, 1893, 629) being employed for this purpose.

When ethyl *β*-hydroxy-*α*-acetylfumarate is treated with diazobenzene chloride at 0°, there is formed, not the possible mixed azo-compound, but *β*-ethyl oxalacetatephenylhydrazone, which, when treated with phenylhydrazine and sodium acetate, dissolved in cold alcohol, is converted into the *α*-isomeride, but when boiled for several minutes with these reagents furnishes the *diphenyldihydrazone*, which is crystalline and melts at 154—155°.

The products obtained by the action of diazobenzene chloride on oxalacetic esters also reduce alkaline solutions of silver nitrate, which is in favour of the hydrazone constitution assigned to them. When ethyl acetoxyfumarate is treated with diazobenzene chloride in presence of acetic acid, there are formed *ethyl diphenylformazylloxalate*,

$\text{NPh}\cdot\text{NC}\cdot\text{N}\cdot\text{NHPh}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$, and a substance which crystallises from benzene, is insoluble in alcohol, and melts at $129\text{--}130^\circ$. T. A. H.

Action of Alcohols on the Tetrazonium Chlorides derived from Benzidine and *o*-Tolidine J. H. C. WINSTON (*Amer. Chem. J.*, 1904, 31, 119—142).—When *m*-ditolyltetrazonium chloride is treated with methyl alcohol, *m*-ditolyl is not obtained, but *dimethoxy-m-ditolyl*, $\text{C}_{14}\text{H}_{12}(\text{OMe})_2$, is produced, which crystallises in silvery leaflets, melts at 145.5° , is soluble in hot alcohol, and yields a *tetranitro*-derivative, melting at 130.5° . By the decomposition of *m*-ditolyltetrazonium chloride with ethyl alcohol, both *m*-ditolyl and diethoxy-*m*-ditolyl are produced. The *tetranitro*-derivative of the latter compound crystallises in rhombs or needles and melts at 142° . If the tetrazonium chloride is treated with sodium methoxide or with a solution of sodium hydroxide in methyl, ethyl, or propyl alcohol, *m*-ditolyl is formed. *m*-Ditolyl is also produced when the tetrazonium chloride is heated with methyl, ethyl, or propyl alcohol in presence of zinc dust, and this reaction affords a good method for its preparation. The action of propyl alcohol on the tetrazonium chloride results in the formation of *m*-ditolyl; no other product could be isolated.

When diphenyltetrazonium chloride is decomposed with methyl alcohol, a trace of diphenyl is formed, but the main product consists of *dimethoxydiphenyl*, which crystallises in pearly plates, melts at 172° , is soluble in hot alcohol, and yields a *tetranitro*-compound melting at 244.6° . By the action of ethyl alcohol, propyl alcohol, or sodium methoxide on diphenyltetrazonium chloride, diphenyl is produced. Diphenyl is also the only product obtained when the tetrazonium chloride is decomposed with methyl, ethyl, or propyl alcohol in presence of zinc dust. E. G.

Method of Separating Albumins from the White of Birds' Eggs. ALEXEI A. PANORMOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 690—695. Compare Abstr., 1899, i, 654, 655).—The author describes the methods employed by him for isolating the albumins. In addition to those already published, the following two new ones are given: (1) a quicker separation is obtained by evaporating the solution, not at the ordinary temperature, but at $37\text{--}40^\circ$. (2) For differentiating albumins, it is proposed: (*a*) to determine the nitrogen content of a given volume of the solution and (*b*) to measure the optical rotation in a 100 mm. tube, and then to calculate what the rotation would be if there were 1 gram of proteid nitrogen in 100 c.c. of the solution. The number thus obtained would be very convenient for determining whether two solutions contained the same or different albumins.

T. H. P.

Stimulating Influence of Proteid Matter on the Oxidation Induced by Manganese. AUGUSTE TRILLAT (*Compt. rend.*, 1904, 138, 94—96).—The action of a manganous salt in alkali solution as a carrier of oxygen (compare this vol., ii, 38) is largely increased by the addition of a small quantity of proteid matter such as white of egg. The exciting action of the albumin is more apparent at the

beginning of the operation, and falls off with the time, thus in two comparative series of experiments the ratios of the amounts of oxygen absorbed in a given time by gallic acid in an alkaline solution of a manganous salt with and without the addition of egg-albumin were as follows: after 10 minutes, 10; after 32 minutes, 8; after 1 hour, 3.5; after 2 hours, 2.5; after 4 hours, 1.9.

The stimulating influence of albumin on manganese as a carrier of oxygen is to be attributed to its tendency to prevent the precipitation of the manganese dioxide, which is thus maintained in a colloidal state, and is consequently more chemically active.

Beyond a certain limit, an increase in the amount of albumin does not accelerate the oxidation, the maximum effect is produced when one part of albumin is added to 1000 parts of the mixture, and the addition of mercuric chloride, arsenic acid, prussic acid, formaldehyde, &c., has a paralysing effect similar to that observed in the case of solutions not containing albumin. Other proteids, such as horse-serum, and colloids, such as gelatin, dextrin, and gum arabic, have given very variable results.

M. A. W.

Enzymes which induce Fermentation isolated from the Cells of the Higher Animals. JULIUS STOKLASA and F. CZERNÝ (*Ber.*, 1903, 36, 4058—4069. Compare *Abstr.*, 1903, ii, 320).—The authors show that the juices expressed from muscles, cows' liver, and cows' lungs respectively contain an enzyme which effects the alcoholic fermentation of dextrose and other sugars; it is also shown that the fermentation observed is not due to bacterial action.

The method of obtaining the enzymes in question is described. The freshly prepared juice has very slight glycolytic properties and does not cause alcoholic fermentation. When an antiseptic is not added to the juice, the proteolytic enzymes and bacteria present completely destroy the enzyme which is capable of causing alcoholic fermentation. A mixture of absolute alcohol and ether was added to the cell-free juice, the resulting precipitate being then drained off and dried at 25—30°. After 14 days, the enzymes present in this solid almost entirely lose their property of fermenting sugar.

The freshly prepared solid was added to 10—15 per cent. sterilised aqueous solutions of dextrose, lævulose, galactose, sucrose, maltose, and lactose respectively, thymol (or toluene) being also added to prevent bacterial growth. The amount of carbon dioxide formed was determined after intervals of 12, 36, and 60 hours. The evolution of carbon dioxide was very marked and in many cases started vigorously immediately after the addition of the enzyme. Control experiments conclusively proved that the fermentation observed in the solutions containing thymol or toluene was not induced by bacteria. The enzyme action was found to start and to be completed much more quickly than the bacterial action.

The enzymes, obtained both from plants and animals, can be heated at 100° from 4 to 6 hours without entirely losing their fermenting power.

The solutions were acid in reaction when the fermentation had ceased, lactic acid being one of the products. In the case of an

enzyme prepared from lungs, it is proved, for the first time, that by the anaërobic respiration of animal organs a certain amount of lactic acid is formed. A. McK.

The Reputed Alcoholic Fermentation of Animal Tissues. F. BATELLI (*Compt. rend.*, 1903, 137, 1079—1080).—Stoklasa and his pupils claim to have extracted from the tissues of higher animals an enzyme which is capable of inducing alcoholic fermentation (compare Abstr., 1903, ii, 321; this vol, ii, 61). Cohnheim (*Centr. Physiol.*, 17, No. 17) maintains that the fermentation is to be attributed to the presence of micro-organisms, and the results described in this paper support his view. The author finds (1) if 1 per cent. of an antiseptic such as thymol, chloroform, sodium fluoride, potassium arsenite, or salicylic acid is added to the sugar solution containing the extract of the animal tissue no alcoholic fermentation takes place, as Simacek has already shown; (2) if the quantity of the antiseptic is reduced to 0.2 per cent. of sodium fluoride or of salicylic acid, fermentation occurs with the formation of carbon dioxide, alcohol, and butyric acid; (3) the microscopical examination of these fermented solutions reveals the presence of bacteria in the form of mobile rods or chains of cocci. M. A. W.

Amylo-coagulase. A. BOLDIN (*Compt. rend.*, 1903, 137, 1080—1082. Compare Wolff and Fernbach, this vol., i, 111).—Amylo-coagulase partially precipitates amylase with starch, the precipitated amylase retaining some of its activity. The diastasic activity of the solution diminishes rapidly in consequence of the precipitation of the amylase. N. H. J. M.

Some Organo-magnesium Derivatives of Dihalogen Substituted Aromatic Hydrocarbons. Action of Carbon Dioxide. F. BODROUX (*Bull. Soc. chim.*, [iii], 31, 24—30).—The action of magnesium on the dihalogen derivatives of benzene yields compounds of the type $C_6H_4X \cdot MgX$, together with small amounts of a diphenyl halogen derivative. *p*-Dibromobenzene and *p*-chlorobromobenzene yielded magnesium *p*-bromophenyl bromide and magnesium *p*-chlorophenyl bromide respectively. When treated with carbon dioxide, the former of these gave *p*-bromobenzoic acid and di-*p*-bromobenzophenone, which crystallises in colourless plates, melts at 172°, and gives an oxime melting at 150°; the chlorine derivative gave *p*-chlorobenzoic acid and di-*p*-chlorobenzophenone, which forms colourless plates melting at 145°; the oxime melts at 135°. S. S.

Organic Chemistry.

Action of Nitric Acid on Acetylene. LUIGI MASCARELLI (*Gazzetta*, 1903, 33, ii, 319—324. Compare Baschieri, *Abstr.*, 1900, 534; 1902, i, 197; Testoni and Mascarelli, *Abstr.*, 1901, i, 494).—The “explosive compound” formed, amongst other substances, on slowly passing acetylene through nitric acid of sp. gr. 1.52, has the composition $C_4H_2O_7N_6$, and, when heated with potassium hydroxide solution, liberates ammonia. On being heated with light petroleum, it decomposes, apparently according to the equation $C_4H_2O_7N_6 = C_4H_2O_3N_4 + N_2O_4$, giving the crystalline substance $C_4H_2O_3N_4$, which has already been described; a small quantity of an oily liquid boiling at 135—140° under 55 mm. pressure is also formed, which, on analysis, gives numbers agreeing with the formula $C_{12}H_{22}O_3N_2$, although the purity of this substance cannot be guaranteed.

The “neutral liquid” formed during the foregoing nitration, after being purified by repeated distillation under diminished pressure, boils at 112° under 40 mm. pressure, and has the composition $C_6H_4O_6N_4$; it is insoluble in acids and alkalis, and evolves ammonia on prolonged heating with aqueous potassium hydroxide.

The monobasic acid, $C_4H_3O_3N$, does not apparently contain the NO_2 group, as it fails to respond to Limpricht's test; it is not reduced by stannous chloride, and does not liberate ammonia with potassium hydroxide. With phenylhydrazine, it gives not a phenylhydrazone, but merely the phenylhydrazine salt, $NH_2 \cdot NHPb, C_4H_3O_3N$, which crystallises from alcohol in white leaflets and melts and decomposes at 176°.

W. A. D.

Action of Reduced Nickel on the Halogen Compounds of the Fatty Series in the Presence of Hydrogen. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1904, 138, 407—409).—A mixture of hydrogen and the vapour of the halogen compound was passed over finely-divided nickel heated at a suitable temperature. The primary alkyl chlorides are attacked at about 250°; as a rule, the first products of reaction are hydrogen chloride and an unsaturated hydrocarbon, but in most instances these unite in the cooler part of the apparatus, giving a small quantity of a tertiary chloride. Thus, *isobutyl* chloride gives hydrogen chloride, *isobutylene*, and *tert.*-butyl chloride; *isoamyl* chloride gives amylene, hydrogen chloride, and the corresponding tertiary chloride. Methyl chloride behaves differently; it gives hydrogen, carbon, and hydrogen chloride. The primary alkyl bromides are attacked at a slightly higher temperature than the chlorides, but the products are analogous. Primary alkyl iodides are decomposed at about 360°, methyl and ethyl iodides giving methane and ethane respectively. Dihalogen derivatives are completely destroyed with formation of carbon, hydrogen, and halogen acid. $\beta\beta$ -Dichloropropane behaves differently; it gives a mixture of α - and β -chloropropylenes at

210°. Chloroform gives carbon and hydrogen chloride; carbon tetrachloride yields hexachloroethane as follows: $2\text{CCl}_4 + \text{H}_2 = \text{C}_2\text{Cl}_6 + 2\text{HCl}$. With a large excess of hydrogen, the hexachloroethane loses halogen, giving tetrachloroethylene, $\text{C}_2\text{Cl}_6 + \text{H}_2 = \text{C}_2\text{Cl}_4 + 2\text{HCl}$; in presence of a still greater excess of hydrogen, carbon and hydrogen chloride are formed. S. S.

Polymerism and Desmotropy of Trimethylethylene Nitrosobromide (β -Bromo- γ -nitroso- β -methylbutane). JULIUS SCHMIDT and FRITZ LEIPPRAND (*Ber.*, 1904, 37, 532—545).—Bis- β -bromo- γ -nitroso- β -methylbutane, $[\text{CMe}_2\text{Br}\cdot\text{CHMe}\cdot\text{NO}]_2$, prepared by the action of fuming hydrobromic acid on a mixture of amyl nitrite and amylene, forms glistening, snow-white, rhombic tablets, melts to a bluish-green liquid when rapidly heated to 67° , and can be crystallised from ethyl alcohol or light petroleum if care is taken to start with hot solvent and cool as soon as the nitroso-compound has dissolved. The solutions are at first colourless, but develop a blue colour, gradually at the ordinary temperature, but immediately on warming; after the colour due to depolymerisation has developed, isomeric change sets in and the nitroso-compound soon passes into the colourless *isonitroso*-compound. Molecular weight determinations in the colourless bis-nitroso-solutions gave $M = 386, 375, 359$, and 350 , calc. 360 , but after the colour had developed, the molecular weight in freezing benzene was found to be $M = 290$. β -Bromo- γ -nitroso- β -methylbutane was obtained only as a blue oil, and attempts at reduction gave much ammonia and very little amine base. *Trimethylethylene isonitrosobromide* [methyl- β -bromo-isopropylketoxime], $\text{CMe}_2\text{Br}\cdot\text{CMe}\cdot\text{NOH}$, can be prepared by heating the nitroso-compound in a thin-walled test-tube over a bare flame until it melts, and then stirring the mass during about 10 minutes with the test-tube in a water-bath at 48° , but if great care is not taken an explosive decomposition takes place; it can also be prepared by boiling a dry ethereal solution of the nitroso-compound until the blue colour has developed and disappeared; the oxime crystallises from light petroleum in stout, white prisms, melts at 78 — 79° , and decomposes, liberating gas, at 140° ; it has a penetrating odour, and does not give Liebermann's reaction, but gives an intense red coloration with ferric chloride. The *benzoyl* derivative, $\text{CMe}_2\text{Br}\cdot\text{CMe}\cdot\text{NOBz}$, crystallises from alcohol in colourless flakes and melts at 70 — 71° to a colourless liquid. The *p*-nitrobenzoyl derivative forms glistening, white needles and melts at 105° . The *methyl* ether, $\text{CMe}_2\text{Br}\cdot\text{CMe}\cdot\text{NOMe}$, prepared by means of diazomethane, forms a pale yellow oil of pleasant odour, which decomposes when distilled even under diminished pressure. The *phenylurethane*, $\text{CMe}_2\text{Br}\cdot\text{CMe}\cdot\text{N}\cdot\text{O}\cdot\text{CO}\cdot\text{NHPh}$, prepared by the action of phenylcarbimide, crystallises from alcohol in colourless prisms and melts at 88 — 89° . Hydrochloric acid converts the oxime quantitatively into hydroxylamine hydrochloride and methyl hydroxyisopropyl ketone, $\text{HO}\cdot\text{CMe}_2\cdot\text{COMe}$, whilst chlorine, acting on the oxime suspended in cold hydrochloric acid, converts it into $\beta\gamma$ -dichloro- γ -nitroso- β -methylbutane, $\text{CMe}_2\text{Cl}\cdot\text{CMeCl}\cdot\text{NO}$, a compound which separates in deep blue needles, coloured very much like copper sulphate crystals, melts at 119 — 120° , and does not appear to exist in a bimolecular form. Potass-

ium hydroxide converts the oxime into a blue oil, which rapidly passes into a colourless mass, the action being apparently that represented by the equation $\text{CMe}_2\text{Br}\cdot\text{CMe}\cdot\text{N}\cdot\text{OH} \rightarrow \text{HBr} \rightarrow \text{CMe}_2\cdot\text{CMe}\cdot\text{NO} \rightarrow [\text{CMe}_2\cdot\text{CMe}\cdot\text{NO}]_x$; the polymeric γ -nitroso- β -methylbutylene separates from ethyl acetate as a colourless powder, which softens at 140° and melts at 145° to a colourless liquid. T. M. L.

Tetramethylethylenenitrosobromide [β -Bromo- γ -nitroso- β - γ -dimethylbutane]. JULIUS SCHMIDT and FRITZ LEIPPRAND (*Ber.*, 1904, 37, 545—549).— β -Bromo- γ -nitroso- β - γ -dimethylbutane, $\text{CMe}_2\text{Br}\cdot\text{CMe}_2\cdot\text{NO}$,

forms a powder of the colour of copper sulphate crystals, has a camphor-like and somewhat penetrating odour, is extraordinarily volatile, and when boiled with water partially vaporises, and is partially converted into β - γ -dimethyl- Δ^6 -butylene, hydrogen bromide, and nitrous acid; it has a normal molecular weight in freezing ethylene dibromide; it does not give Liebermann's reaction, but liberates iodine from potassium iodide, and precipitates silver bromide from alcoholic silver nitrate; under no conditions was it possible to bring about isomeric change, but exposure to sunlight converts it into β - γ -dimethyl- Δ^6 -butylene dibromide, $\text{CMe}_2\text{Br}\cdot\text{CMe}_2\text{Br}$. Cold aqueous potassium hydroxide has no action on the nitroso-compound, but on warming, the original hydrocarbon is regenerated. β - γ -Tribromo- β -methylbutane (tribromotrimethylethane), $\text{CMe}_2\text{Br}\cdot\text{CMeBr}_2$, produced by the action of nitrosyl bromide or of bromine on bromomethyl- Δ^6 -butylene, crystallises from alcohol in colourless needles, has a strong camphor-like odour, and is so volatile that its melting point could not be determined.

T. M. L.

Trichloroisopropyl Alcohol. LOUIS HENRY (*Compt. rend.*, 1904, 138, 205—206).— α -Trichloroisopropyl alcohol, readily obtained by Grignard's synthesis from anhydrous chloral and magnesium methiodide (compare Grignard, *Abstr.*, 1901, i, 679), is a white, crystalline substance melting at 50 — 51° , and boiling at 161.8° under 773 mm. pressure [Thurnlackh, *Abstr.*, 1882, 295, gives 49° and 155° for these constants]. The three alcohols of which this forms the middle term exhibit the same regularity in melting points and boiling points which obtains in other homologous series (compare *Abstr.*, 1901, i, 128; 1903, i, 2; ii, 8).

M. A. W.

Action of Sulphuric Acid on Butane-1:3-diol. FRIEDRICH BAUER (*Monatsh.*, 1904, 25, 1—11).—The action of dilute sulphuric acid on β -butylene glycol (butane- α - γ -diol) in a sealed tube at 190° yields the following products:—(1) *n*-Butaldehyde. (2) Methyl ethyl ketone; these two compounds are to be expected, according to Lieben's rule (*Abstr.*, 1902, i, 336) for the action of dilute sulphuric acid on glycols in which the two alcohol chains are separated by a hydrocarbon group. (3) As main product, a compound, $\text{C}_8\text{H}_{14}\text{O}$, obtained as a yellow liquid boiling at 98 — 105° under 20 mm. pressure, and under the ordinary pressure at 175 — 185° with slight decomposition; it is readily soluble in ether and slightly so in water, and unites with 2 atoms of bromine; with zinc ethyl, it yields a dark yellow oil boiling

at about 170° and having an unpleasant odour; its *oxime*, $C_8H_{15}ON$, is a yellow liquid boiling at 180° . (4) A *compound*, $C_{12}H_{20}O$, which is a green, viscous liquid possessing but a slight odour and boiling at about 200° under 20 mm. pressure; it is readily soluble in alcohol or ether and neither combines with bromine nor yields an oxime; it is formed either by the condensation of 3 mols. of butane- α -diol with elimination of $5H_2O$ or by the condensation of *n*-butaldehyde or methyl ethyl ketone.

T. H. P.

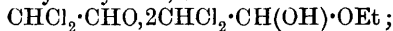
$\alpha\beta$ -Trichloroethyl Ether. GIUSEPPE ODDO and EFISIO MAMELI (*Gazzetta*, 1903, 33, ii, 373—419).— *$\alpha\beta$ -Trichloroethyl ether*,



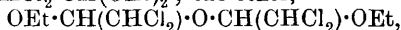
forms 80 per cent. of the product obtained by chlorinating *$\alpha\beta$ -dichloroethyl ether* in a reflux apparatus with 1 mol. of chlorine at the temperature of boiling saturated salt solution; when purified by fractional distillation under atmospheric pressure, it boils at 170 — 175° and has a sp. gr. 1.3303 at 14° . When boiled for 250 hours, it loses hydrogen chloride, giving principally ethyl *$\beta\beta$ -dichlorovinyl ether*, $CCl_2 \cdot CH \cdot OEt$ (Godefroy, *Abstr.*, 1886, 606), which boils at 144 — 146° , and a *polymeride* of this, $(C_4H_6OCl_2)_2$, which boils at 187 — 192° under 30 mm. pressure and is unsaturated.

$\beta\beta$ -Dichloro- $\alpha\beta$ -dibromoethyl ether, $CCl_2Br \cdot CHBr \cdot OEt$, prepared by the addition of bromine to *$\beta\beta$ -dichlorovinyl ethyl ether*, boils at 127 — 132° under 25—30 mm. pressure. *$\alpha\beta\beta$ -Trichloroethyl ether* is not changed when heated in a sealed tube for several hours at 215° , but at 230 — 240° is resolved principally into dichloroacetaldehyde and ethyl chloride; the same products are formed, but in small quantity, when dry hydrogen chloride is passed through the trichloroether for 6 hours at 110° , and when *$\alpha\beta\beta$ -trichloroethyl ether* is distilled with concentrated sulphuric acid the yield of dichloroacetaldehyde is 25 per cent. that of theory; this gives a better method of preparing the chlorinated aldehyde than that of Grimaux and Adam (*Bull. Soc. chim.*, 1880, [ii], 34, 29). Conversely, *$\alpha\beta\beta$ -trichloroethyl ether* can be synthesised by passing hydrogen chloride into an alcoholic solution of dichloroacetaldehyde, the compound, $CHCl_2 \cdot CH(OH) \cdot OEt$, probably being formed as an intermediate product.

When boiled with water, *$\alpha\beta\beta$ -trichloroethyl ether* gives a complex mixture which fractional distillation resolves into acetaldehyde, *$\beta\beta$ -dichloroacetaldehyde hydrate*, the substance



dichloroacetal, $CHCl_2 \cdot CH(OEt)_2$; the ether,



derived from the alcoholate of dichloroacetaldehyde, and the acetal, $OEt \cdot CH(CHCl_2) \cdot O \cdot CH(CHCl_2) \cdot O \cdot CH(CHCl_2) \cdot OEt$, formed from the condensation of 1 mol. of chloroacetaldehyde hydrate and 2 mols. of dichloroacetaldehyde alcoholate. The mechanism of the reaction is discussed. The following substances of those mentioned are new or hitherto have been described incorrectly.

Dichloroacetaldehyde hydrate, $CHCl_2 \cdot CH(OH)_2$, forms large, colourless, quadrangular plates, melts at 55 — 56° , and boils at 96.5 — 97.5° ; Fritsch and Schumacher's dihydrate, $CHCl_2 \cdot CHO, 2H_2O$ (*Abstr.*, 1894,

i, 485), is really the substance, $\text{CHCl}_2 \cdot \text{CHO} \cdot 2\text{CHCl}_2 \cdot \text{CH}(\text{OH}) \cdot \text{OEt}$, which boils at $110-111^\circ$ and is probably not a definite compound but a mixture of constant boiling point, as the molecular weight, determined by the cryoscopic method, has a value one-third of the calculated. On keeping, it decomposes giving dichloroacetaldehyde hydrate, dichloroacetal, and the solid melting at 82° , and with alcohol it forms dichloroacetaldehyde alcoholate, $\text{CHCl}_2 \cdot \text{CH}(\text{OH}) \cdot \text{OEt}$, which boils at $109.5-111^\circ$ and has a sp. gr. 1.314 at 26° ; Fritsch and Schumacher's "dichloroacetaldehyde alcoholate" was a mixture.

The ether, $[\text{OEt} \cdot \text{CH}(\text{CHCl}_2)]_2\text{O}$, boils at $183-188^\circ$; it was not obtained pure.

The acetal, $\text{OEt} \cdot \text{CH}(\text{CHCl}_2) \cdot \text{O} \cdot \text{CH}(\text{CHCl}_2) \cdot \text{O} \cdot \text{CH}(\text{CHCl}_2) \cdot \text{OEt}$, crystallises from light petroleum in long, white needles and melts at $82-84^\circ$.

The action of alkalis on $\alpha\beta\beta$ -trichloroethyl ether gives complex products which are still being investigated; in no case is ethyl dichlorovinyl ether formed.

On boiling $\alpha\beta\beta$ -trichloroethyl ether with alcohol, it gives dichloroacetal, $\text{CHCl}_2 \cdot \text{CH}(\text{OEt})_2$; with methyl alcohol, $\beta\beta$ -dichloro- $\alpha\alpha$ -dimethoxyethane, $\text{CHCl}_2 \cdot \text{CH}(\text{OMe})_2$, boiling at $166-168^\circ$, is obtained, and $\beta\beta$ -dichloro- α -methoxy- α -ethoxyethane, which boils at $173-175^\circ$, being partly decomposed into $\beta\beta$ -dichloro- $\alpha\alpha$ -dimethoxyethane and dichloroacetal.

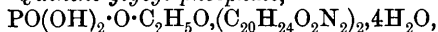
By sodium methoxide in ethereal solution, $\alpha\beta\beta$ -trichloroethyl ether is converted into ethyl dichlorovinyl ether, and by boiling propyl alcohol, into $\beta\beta$ -dichloro- $\alpha\alpha$ -dipropoxyethane, boiling at $212-214^\circ$, and $\beta\beta$ -dichloro- α -ethoxy- α -propoxyethane, which boils at $202-204^\circ$; both these substances, when heated with concentrated sulphuric acid, give dichloroacetaldehyde.

W. A. D.

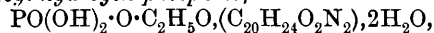
***n*-Propyl Ether and the Products of its Direct Chlorination.** GIUSEPPE ODDO and GUIDO CUSMANO (*Gazzetta*, 1903, 33, ii, 419-427).—Details are given for preparing *n*-propyl ether by the action of sulphuric acid on *n*-propyl alcohol, and of ferric chloride on the same substance. It boils at $89-91^\circ$, and on passing chlorine through it at the ordinary temperature until an increase of weight is obtained corresponding with two atoms of chlorine, a mixture of *dichloro*- and *trichloro-n-propyl ethers* is formed. The former, which boils at 80° under 15 mm. and at 176° under 762 mm. pressure, is perhaps identical with Brochet's compound (*Abstr.*, 1896, i, 114); the latter boils at $133-138^\circ$ under 2-3 mm. pressure, and is decomposed when distilled under atmospheric pressure. W. A. D.

Phosphoric Esters of Ethylene Glycol. PAUL CARRÉ (*Compt. rend.*, 1904, 138, 374-375).—When molecular proportions of phosphoric acid and ethylene glycol are heated for 10 hours at $140-145^\circ$ under 15-18 mm. pressure, 89.9 per cent. of the phosphoric acid is esterified, the product consisting of 3.5 per cent. of the tri-ester, 42.4 per cent. of the di-ester, and 44 per cent. of the mono-ester; by increasing the quantity of glycol to two molecular proportions, the yield of the tri-ester can be raised to 14.5 per cent. The di- and tri-esters are converted into the mono-ester by hydrolysis with water, and as they present no differences in solubility to the mono-ester they have not been isolated. The mono-ester, *glycol*

dihydrogen phosphate, $2\text{PO}(\text{OH})_2 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}, \text{H}_2\text{O}$, is isolated by decomposing its lead salt with hydrogen sulphide. *Barium glyceryl phosphate*, $\text{PO}(\text{O}_2\text{Ba}) \cdot \text{O} \cdot \text{C}_2\text{H}_5\text{O}, \text{H}_2\text{O}$, loses a molecular proportion of water at 180° . *Quinine glyceryl phosphate*,



and *quinine glyceryl hydrogen phosphate*,



crystallise in thin needles, but effloresce at the ordinary temperature losing one molecular proportion of water. M. A. W.

Preparation of the Chlorides and Anhydrides of Organic Acids. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 146690).—Chlorosulphonic acid reacts with organic acids to form sulpho-derivatives; when, however, carboxylic acids or their salts are warmed with metallic chlorosulphonates, the chlorides of the organic acids are produced: $\text{RCO}_2\text{Na} + \text{ClSO}_3\text{Na} = \text{RCOCl} + \text{Na}_2\text{SO}_4$. Acid anhydrides are obtained when the proportion of organic acid is doubled. The chlorosulphonates are prepared by heating chlorosulphonic acid with the calculated quantity of the corresponding metallic chloride at 150° , moisture being excluded. The preparation of acetyl and benzoyl chlorides, and of acetic and benzoic anhydrides, is described. C. H. D.

Electrolysis of Fused Organic Salts. ERNST BERL (*Ber.*, 1904, 37, 325—331).—It is difficult to obtain satisfactory results on electrolysis of fused organic salts, because nearly all begin to decompose in absence of a current at a temperature slightly above their melting points; moreover, they are such bad conductors that the heat produced by their resistance to a current intensifies this decomposition. When fused sodium acetate is electrolysed with a current of 0.2 ampere at 8 volts, a gaseous mixture consisting of 20.86 per cent. of carbon dioxide, 43.56 per cent. of hydrogen, and 25.92 per cent. of methane is obtained; it is shown that the hydrocarbon, which is here liberated at the cathode instead of at the anode, as in solution (compare Lassar-Cohn, *Abstr.*, 1889, 1056), is produced by a secondary change, namely, the action of the metallic sodium on the fused salt, which gives rise also to sodium carbonate and carbon. Potassium acetate, under similar conditions, gives the same products, whilst potassium propionate gives 70.4 per cent. of hydrogen and 20.8 per cent. of ethane. Schall and Klien's observation (*Abstr.*, 1889, i, 425) of the production of nitrobenzene from potassium *o*-nitrobenzoate is confirmed and shown to be due similarly to the action of metallic potassium on the fused salt. W. A. D.

Salts of Antimony with Organic Acids. II. EDUARD JORDIS and WILHELM MEYER (*Zeit. angew. Chem.*, 1904, 17, 169—175, 204—208, 236—239. Compare this vol., i, 216).—Antimony acetate, formed by heating antimony oxide (1 mol.) with acetic anhydride (5 mols.) until all is dissolved, is crystalline, and is unstable at the ordinary temperature. The solubility of antimony oxide in formic, acetic, chloroacetic, dichloroacetic, trichloroacetic, propionic, butyric, oxalic, malonic, succinic, maleic, fumaric, glycollic, lactic, tartaric,

citric, benzoic, salicylic, *p*-nitrosalicylic, and gallic acids respectively and in tannin has been examined. A. McK.

Chlorination by means of Sulphuryl Chloride. ALFRED WOHL (D.R.-P. 146796).—Sulphuryl chloride may conveniently be employed as a chlorinating agent by carrying out the operation in a closed vessel under pressure. Air is pumped into the vessel at the commencement of the heating, and the evolved gases pass through a condenser, escaping by a valve under the desired constant pressure. Chloroacetic acid is thus prepared by heating acetic acid with sulphuryl chloride at 115–120° under 4–5 atmospheres' pressure. C. H. D.

Bromopivalic Acid [β -Bromo- $\alpha\alpha$ -dimethylpropionic Acid] and its Derivatives. EDMOND E. BLAISE and L. MARCILLY (*Bull. Soc. chim.*, 1904, [iii], 31, 155–160. Compare Reformatsky, *Abstr.*, 1890, 1096).—When β -hydroxy- $\alpha\alpha$ -dimethylpropionic acid (this vol., i, 219) (1 mol.) is treated with phosphorus pentabromide (2 mols.), there are formed β -bromo- $\alpha\alpha$ -dimethylpropionic acid and phospho-di- β -hydroxy- $\alpha\alpha$ -dimethylpropionic acid. The former is crystalline, melts at 40·5–41°, distils at 143–145° under 33 mm. pressure, and is very soluble in alcohol or ether. On exposure to air, the crystals liquefy and darken. When treated with potassium hydroxide, dissolved in water, the corresponding hydroxy-acid is reproduced. The *ethyl* ester, obtained either by esterifying the acid or by treating ethyl hydroxydimethylpropionate with phosphorus pentabromide, boils at 89–90° under 25 mm. pressure.

Phospho-di- β -oxy- $\alpha\alpha$ -dimethylpropionic acid,



crystallises from ethyl acetate in white, cauliflower-like masses of slender needles, melts, when rapidly heated, at 110–120°, but when slowly heated or previously dehydrated, at 148°; the acid is not decomposed when warmed with sulphuric acid or with a 50 per cent. aqueous solution of potassium hydroxide, but is attacked by fused sodium nitrate, forming phosphoric acid. The *potassium* salt, $(\text{C}_{10}\text{H}_{16}\text{O}_8\text{PK}_3)_2\cdot 5\text{H}_2\text{O}$, prepared by neutralising the acid with potassium hydroxide, using phenolphthalein as indicator, forms colourless crystals. *Ethyl hydrogen phospho-di-oxydimethylpropionate*, $\text{OH}\cdot\text{PO}(\text{O}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et})_2$, obtained by the action of phosphorus pentabromide on ethyl hydroxydimethylpropionate, is a colourless liquid, which cannot be distilled. There is also formed in this reaction a small quantity of an oily substance, which may be the normal ester, $\text{PO}(\text{O}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et})_3$.

T. A. H.

Theory of Saponification. JULIUS LEWKOWITSCH (*Ber.*, 1904, 37, 884. Compare *Abstr.*, 1903, i, 547; this vol., i, 6, 216).—*Polemical*: a reply to Balbiano. J. J. S.

Conversion of Paraffins into Alcohols and Fatty Acids during the Saponification of Spermaceti. G. REALE (*Chem. Zeit.*, 1904, 28, 242–243).—When spermaceti is saponified in the presence

of petroleum, the hydrocarbons of the petroleum are at the same time attacked by the alkali hydroxide with formation of an alcohol, the corresponding acid and hydrogen. Butane, for instance, is transformed into butyl alcohol, potassium butyrate, and hydrogen.

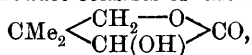
A. McK.

Biochemical Syntheses of Olein and some Esters. HENRI POTTEVIN (*Compt. rend.*, 1904, 138, 378—380. Compare Abstr., 1903, ii, 494).—In addition to the mono-olein already described, tri-olein is prepared by the action of the pancreatic ferment on mixtures of the mono-olein and oleic acid at 36°; it is a neutral fat, solidifies at about 0°, and has a sp. gr. 0.915 at 15°. This esterifying action of the pancreatic ferment has also been extended to alcohols and acids other than glycerol and oleic acid; thus, under suitable conditions of concentration and temperature, methyl, ethyl, and *iso*amyl alcohols react with oleic acid; stearic acid with amyl alcohol; acetic, butyric, and propionic acids with amyl alcohol, provided the quantity of alcohol present is not greater than 100 grams to 8 grams of the acid. *d*- and *l*-Lactic acids and benzoic acid are not sensitive to the action of the ferment, in fact, the esterification of a mixture of oleic acid and amyl alcohol is retarded by 0.4 per cent. of lactic acid, whilst 0.8 per cent. stops it altogether.

isoAmyl oleate is a neutral, odourless liquid, which does not solidify at 0° and has a sp. gr. 0.897 at 15°. *isoAmyl stearate* is a neutral, white solid melting at 21°, is insoluble in water, soluble in ether, and can be obtained in the form of small, square, crystalline plates from a solution of warm alcohol.

M. A. W.

Action of Hydrogen Cyanide on Methyloldimethylacetaldehyde. ERHARD GLASER (*Monatsh.*, 1904, 25, 46—54).—On treating methyloldimethylacetaldehyde with hydrogen cyanide and hydrolysing the impure cyanohydrin thus obtained with dilute hydrochloric acid, the main product consists of the *hydroxylactone*,

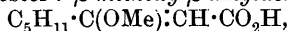


which solidifies to a drusy mass of prismatic needles melting at 55° and boiling at 115—117°; it is extremely hygroscopic and dissolves readily in water, ether, benzene, chloroform, alcohol, or carbon disulphide; of the corresponding acid, the *calcium* salt, $(\text{C}_6\text{H}_{11}\text{O}_4)_2\text{Ca} \cdot 3\text{H}_2\text{O}$, and the *silver* salt (with $8\text{H}_2\text{O}$) were prepared; the *acetyl* derivative of the lactone, $\text{C}_8\text{H}_{12}\text{O}_4$, is a colourless, almost odourless liquid boiling at 122—125° under 11 mm. pressure. Attempts to reduce the hydroxy-lactone to the corresponding lactone or to α -hydroxy- $\beta\beta$ -dimethylpropionic or $\beta\beta$ -dimethylpropionic acid were unsuccessful.

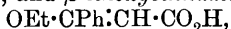
If, in preparing the lactone, the hydrochloric acid solution is left for 2 or 3 days in contact with the ethereal solution of the cyanohydrin, there remain, after removal of the ether, an oily liquid and white, acicular crystals, which do not contain nitrogen, melt at 156°, and are readily soluble in ether. On heating the oily liquid with hydrochloric acid, it yields a substance separating from ether in rhombic crystals melting at 182°.

T. H. P.

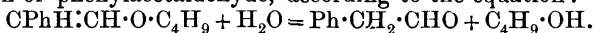
Alkyloxyalkylethylenic Acids and Hydrocarbons. CHARLES MOUREU (*Compt. rend.*, 1904, 138, 286—289. Compare next page).—The author has prepared the following acids by hydrolysis of the corresponding ester: *β-methoxy-β-amylacrylic acid*,



melting at $54\cdot5^\circ$, *β-ethoxy-β-amylacrylic acid*, $\text{C}_5\text{H}_{11}\cdot\text{C}(\text{OEt})\cdot\text{CH}\cdot\text{CO}_2\text{H}$, melting at 74° , *β-propoxy-β-amylacrylic acid*, $\text{C}_5\text{H}_{11}\cdot\text{C}(\text{OPr}^a)\cdot\text{CH}\cdot\text{CO}_2\text{H}$, melting at 58° , *β-methoxy-β-hexylacrylic acid*, $\text{C}_6\text{H}_{13}\cdot\text{C}(\text{OMe})\cdot\text{CH}\cdot\text{CO}_2\text{H}$, melting at $55\cdot5^\circ$, *β-methoxycinnamic acid*, $\text{OMe}\cdot\text{CPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, decomposing at about 180° , and *β-ethoxycinnamic acid*,



which decomposes at about 160° . These acids are not hydrolysed by ferric chloride, and therefore give no coloration with that reagent; they are readily hydrolysed by warm dilute sulphuric acid with the formation of the corresponding ketone, according to the equation $\text{C}_5\text{H}_{11}\cdot\text{C}(\text{OMe})\cdot\text{CH}\cdot\text{CO}_2\text{H} + \text{H}_2\text{O} = \text{C}_5\text{H}_{11}\cdot\text{CO}\cdot\text{CH}_3 + \text{MeOH} + \text{H}_2\text{O} + \text{CO}_2$; and on being heated, lose carbon dioxide and form the corresponding alkyloxyalkylethylene, of which the following were prepared: *ββ-methoxy-Δ^α-heptylene*, $\text{C}_5\text{H}_{11}\cdot\text{C}(\text{OMe})\cdot\text{CH}_2$, boiling at $145\cdot5^\circ$, *ββ-ethoxy-Δ^α-heptylene*, $\text{C}_5\text{H}_{11}\cdot\text{C}(\text{OEt})\cdot\text{CH}_2$, boiling at $161\text{--}161\cdot5^\circ$, *ββ-propoxy-Δ^α-heptylene*, $\text{C}_5\text{H}_{11}\cdot\text{C}(\text{OPr}^a)\cdot\text{CH}_2$, boiling at $181\text{--}182^\circ$, *β-methoxy-Δ^α-octylene*, $\text{C}_6\text{H}_{13}\cdot\text{C}(\text{OMe})\cdot\text{CH}_2$, boiling at $166\text{--}168^\circ$, *β-methoxy-β-phenylethylene*, $\text{OMe}\cdot\text{CPh}\cdot\text{CH}_2$, boiling at 197° , and *β-ethoxy-β-phenylethylene*, $\text{OEt}\cdot\text{CPh}\cdot\text{CH}_2$, boiling at $209\text{--}210^\circ$, previously prepared by Claisen (compare *Abstr.*, 1896, i, 464). These compounds are readily hydrolysed by dilute sulphuric acid, yielding the corresponding ketone, thus: $\text{C}_6\text{H}_{13}\cdot\text{C}(\text{OMe})\cdot\text{CH}_2 + \text{H}_2\text{O} = \text{CH}_3\cdot\text{OH} + \text{C}_6\text{H}_{13}\cdot\text{CO}\cdot\text{CH}_3$. Attempts to prepare α-alkyloxy-β-alkylethylenic compounds of the type $\text{CHR}\cdot\text{CH}(\text{OR}')$ by condensing the corresponding alkylacetylene, $\text{CR}:\text{CH}$, with alcohol in the presence of sodium were unsuccessful owing to the transformation of the acetylene into its symmetrical isomeride by the action of the alkali (compare Faworsky, *Abstr.*, 1888, 798), thus, Δ^α-heptinene, $\text{C}_5\text{H}_{11}\cdot\text{C}:\text{CH}$, was converted into Δ^β-heptinene, $\text{C}_4\text{H}_9\cdot\text{C}:\text{CMe}$. Phenylacetylene, however, gives normal condensation products with alcohols in the presence of sodium, and the following compounds were prepared: *α-methoxystyrene*, $\text{CPhH}\cdot\text{CH}\cdot\text{OMe}$, boiling at $210\text{--}213^\circ$, *α-ethoxystyrene*, $\text{CPhH}\cdot\text{CH}\cdot\text{OEt}$, boiling at $225\text{--}226^\circ$, *α-propoxystyrene*, $\text{CPhH}\cdot\text{CH}\cdot\text{OPr}^a$, boiling at $238\text{--}241^\circ$, *α-isobutoxystyrene*, $\text{CPhH}\cdot\text{CH}\cdot\text{OC}_4\text{H}_9$, boiling at $248\text{--}251^\circ$. These compounds are hydrolysed by dilute sulphuric acid with the formation of phenylacetaldehyde, according to the equation:



M. A. W.

β-Aldehydo-esters. EDMOND E. BLAISE and L. MARCILLY (*Bull. Soc. chim.*, 1904, [iii], 31, 160—170).—Previous attempts to prepare β-aldehydo-acids have given rise to the production of the isomeric unsaturated secondary alcohols (Wislicenus, *Abstr.*, 1888, 129, and von Pechmann, *Abstr.*, 1892, 816). When ethyl β-hydroxy-αα-dimethylpropionate (this vol., i, 219) is oxidised with chromic acid in the absence of a solvent, small quantities of a substance giving the

reactions of an aldehyde are produced, but most of the original ester is recovered unchanged. When the oxidation is effected in acetic acid solution at 0° , the principal products are ethyl hydrogen dimethylmalonate, and the *ester*, $\text{CO}_2\text{Et}\cdot\text{CMe}_2\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$, formed by the interaction of this with ethyl hydroxydimethylpropionate, which boils at $156\text{--}157^{\circ}$ under 18 mm. pressure, and on hydrolysis furnishes hydroxydimethylpropionic and dimethylmalonic acids. There is also produced, however, a small quantity of *ethyl formylisobutyrate*, $\text{CHO}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$, which is best isolated as its sodium bisulphite compound. This ester is a colourless, mobile oil with a pronounced aldehydic odour; it boils at $65\text{--}66^{\circ}$ under 20 mm. pressure, has a sp. gr. 0.9834 at $20^{\circ}/4^{\circ}$ and gives the usual aldehyde reactions, but does not give a coloration with ferric chloride. The *semicarbazone* crystallises in needles and melts at $161\text{--}162^{\circ}$.

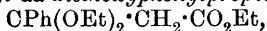
When treated with phenylhydrazine, *ethyl formylisobutyrate* is converted into 1-phenyl-4:4-dimethyl-5-pyrazolone, $\text{NPh}\begin{matrix} \text{N}=\text{CH} \\ | \\ \text{CO}\cdot\text{CMe}_2 \end{matrix}$, which crystallises in needles, melts at 51° , and is very soluble in ether.

Ethyl formylisobutyrate, when hydrolysed by ebullition with dilute sulphuric acid, furnishes isobutaldehyde (the *semicarbazone* forms large leaflets melting at $126\text{--}127^{\circ}$) and carbon dioxide. When hydrolysed with baryta water, there are formed in addition to isobutaldehyde, ethyl isobutyrate and formic acid.

The β -aldehydo-esters resemble the β -ketonic esters, but are less stable than these compounds, owing to the greater reactivity of the formyl radicle as compared with its higher homologues. T. A. H.

Ethyl γ -Chloroacetoacetate. ROBERT LESPIEAU (*Compt. rend.*, 1904, 38, 421—423).—Ethyl γ -chloroacetoacetate is formed by carefully oxidising the ethyl γ -chloro- β -hydroxypropionate with potassium dichromate and sulphuric acid. The ketonic ester may be isolated from the reaction product by means of its insoluble copper derivative, which separates on shaking the oxidation product with aqueous copper acetate. This copper derivative dissolves in hot benzene, and is deposited from the cold medium in green crystals which melt at 168° . Ethyl γ -chloroacetoacetate forms a colourless liquid which boils at 105° under 11 mm. pressure, with considerable decomposition at 205° under the ordinary pressure, and has a sp. gr. 1.23 at 0° . The ester, when added to solutions of ferric salts, develops a deep reddish-violet coloration. S. S.

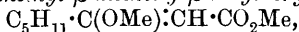
Condensation of Acetylenic Esters with Alcohols. II. CHARLES MOUREU (*Compt. rend.*, 1904, 138, 206—209. Compare *Abstr.*, 1903, i, 698).—The condensation of the acetylenic esters with alcohols to form the corresponding saturated acetal derivatives is a general reaction. *Ethyl aa-diethoxyphenylpropionate*,



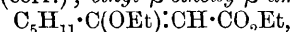
prepared from ethyl phenylpropiolate and ethyl alcohol, boils at 153° (corr.) under 13 mm. pressure, and on saponification yields the corre-

sponding acid in the form of white crystals melting at 68° with evolution of gas; both the acid and its ester are rapidly coloured red by an alcoholic solution of ferric chloride; this is due to the formation of benzoylactic acid by the hydrolytic action of the ferric chloride.

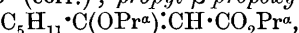
When esters of the above type are heated at about 175° , they readily lose one molecular proportion of alcohol and yield the corresponding ethylenic compound in theoretical quantity; the following compounds were thus prepared: *methyl β -methoxy- β -amylacrylate*,



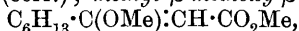
boiling at $232\text{--}233^{\circ}$ (corr.); *ethyl β -ethoxy- β -amylacrylate*,



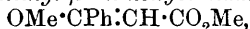
boiling at $253\text{--}253.5^{\circ}$ (corr.); *propyl β -propoxy- β -amylacrylate*,



boiling at $279\text{--}280^{\circ}$ (corr.); *methyl β -methoxy- β -hexylacrylate*,

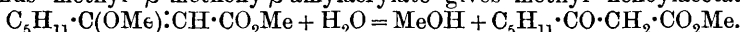


boiling at $245\text{--}248^{\circ}$; *methyl β -methoxycinnamate*,



boiling at $154\text{--}155^{\circ}$ (corr.) under 14 mm. pressure, and *ethyl β -ethoxycinnamate*, $\text{OEt}\cdot\text{CPh}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, boiling at $167\text{--}168^{\circ}$ (corr.) under 16 mm. pressure, previously prepared by Claisen (compare Abstr., 1896, i, 463).

With the exception of the last, these compounds are not readily hydrolysed, and thus give only a feeble coloration with ferric chloride. The four esters of the aliphatic series are readily hydrolysed by warm sulphuric acid yielding the ester of the corresponding β -ketonic acid, thus methyl β -methoxy- β -amylacrylate gives methyl hexoylacetate,



The two esters of the aromatic series give acetophenone on hydrolysis according to the equation: $\text{CPh}(\text{OMe})\cdot\text{CH}\cdot\text{CO}_2\text{Me} + 2\text{H}_2\text{O} = 2\text{MeOH} + \text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}_3 + \text{CO}_2$.
M. A. W.

Baeyer's Tension Theory. ARNOLD F. HOLLEMAN and GERARDUS L. VOERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 410—412).—Since Baeyer's Tension theory is based on qualitative observations only, the authors have considered it from a quantitative standpoint by investigating the relative stability of the anhydrides of saturated dibasic acids with respect to water. The velocity with which those anhydrides are converted into their corresponding acids may be taken as a measure of the tension in the ring. Succinic, glutaric, adipic, pimelic, suberic, azelaic, and sebacic anhydrides were examined, and the velocity of their conversion into acids was measured by the electric conductivity of the solution, the assumption being made that the solution of the anhydride is a non-conductor. As the concentration of the acid, after complete conversion of the anhydride, did not exceed $N/23$ in the velocity measurements, the quantity of water may be taken as constant, and the conversion is unimolecular.

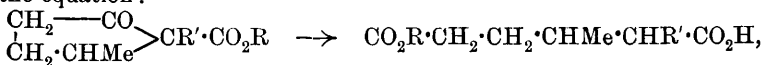
Succinic and glutaric anhydrides only gave satisfactory constants at 25° ; the figures show that the 5-membered ring is more stable than the 6-membered ring. Accurate measurement was not found to be possible in the case of the higher anhydrides, owing to their sparing solubility in water. Moreover, boiling point determinations of the

solutions of the higher anhydrides in acetone show that they are polymerised, whilst succinic and glutaric anhydrides give normal values.

A. McK.

α -Substituted β -Methyladipic Acids. MARCEL DESFONTAINES (*Compt. rend.*, 1904, 138, 209—211).—The author has prepared the following esters of α -substituted cyclopentanonecarboxylates by Dieckmann's method (compare Abstr., 1894, i, 173) from the esters of β -methylcyclopentanonecarboxylate, by the action of alkyl iodides in the presence of sodium wire in anhydrous ether or powdered sodium in toluene: *methyl 1:5-dimethyl-2-cyclopentanone-1-carboxylate*, which boils at 105—106° under 15 mm. pressure and has a sp. gr. 1.065 at 0° and n_D 1.450 at 20°; *ethyl 1:5-dimethyl-2-cyclopentanone-1-carboxylate*, which boils at 112—113° under 15 mm. pressure and has a sp. gr. 1.030 and n_D 1.444 at 19°; *methyl 5-methyl-1-allylcyclopentanone-1-carboxylate*, which boils at 114—115° under 15 mm. pressure; *ethyl 5-methyl-1-allyl-2-cyclopentanone-1-carboxylate*, which boils at 139—141° under 18 mm. pressure (compare Haller and Desfontaines, Abstr., 1903, i, 628); *methyl 5-methyl-1-ethyl-2-cyclopentanone-1-carboxylate*, which boils at 108—110° under 15 mm. pressure and has a sp. gr. 1.073 and n_D 1.456 at 15°; *methyl 5-methyl-1-propyl-2-cyclopentanone-1-carboxylate*, which boils at 138—140° under 22 mm. pressure; *ethyl 5-methyl-1-ethyl-2-cyclopentanone-1-carboxylate*, which boils at 119—120° under 18 mm. pressure; *ethyl 5-methyl-1-propyl-2-cyclopentanone-1-carboxylate*, which boils at 136—137° under 17 mm. pressure; and *ethyl 5-methyl-1-isobutyl-2-cyclopentanone-1-carboxylate*, which boils at 188—190° under 18 mm. pressure.

All these esters are readily saponified by alcoholic potassium hydroxide, yielding the corresponding substituted adipic acid, according to the equation:



and the following new compounds were thus prepared: $\alpha\beta$ -dimethyladipic acid, which boils at 214—216° under 18 mm. pressure, melts at 80°, and forms a dianilide melting at 158°; β -methyl- α -ethyladipic acid, which melts at 97—98°; β -methyl- α -propyladipic acid, which melts at 110°; and β -methyl- α -allyladipic acid, which melts at 104°.

M. A. W.

Condensation of *iso*Butyrylformaldol with Malonic Acid. ARTHUR SILBERSTEIN (*Monatsh.*, 1904, 25, 12—20).—The condensation of *isobutyrylformaldol* with malonic acid in presence of alcoholic ammonia yields: (1) the lactone of γ -dimethylmethylolcrotonic acid, $\text{CMe}_2\left\langle \begin{array}{c} \text{CH}_2-\text{O} \\ \text{CH}\cdot\text{CH} \end{array} \right\rangle \text{CO}$, which separates from alcohol in needles melting at 177° and is soluble in ether, carbon disulphide, or benzene; in freezing benzene, it has double the normal molecular weight; when boiled with barium hydroxide solution, it yields the barium salt of the corresponding hydroxy-acid, $(\text{C}_7\text{H}_{11}\text{O}_3)_2\text{Ba}$; its dibromide, $\text{C}_7\text{H}_{10}\text{O}_2\text{Br}_2$, separates from benzene in crystals melting and decomposing (?) at 152°.

(2) The ammonium salt of the lactonic acid of α -dihydroxy- $\beta\beta$ -dimethylpropylmalonic acid, $\text{CMe}_2 \begin{matrix} \text{CH}_2 - \text{O} \cdot \text{CO} \\ \text{CH}(\text{OH}) \cdot \text{CH} \cdot \text{CO}_2\text{H} \end{matrix}$; the acid crystallises from water in star-shaped aggregates of shining needles melting at 82° and is soluble in ether; its calcium salt was prepared and analysed; oxidation of the acid with alkaline potassium permanganate solution yields malonic and dimethylmalonic acids.

The first product of the condensation of isobutyrylformaldol and malonic acid by means of alcoholic ammonia is the ammonium salt (2), which then loses ammonia, carbon dioxide, and water yielding the lactone (1).
T. H. P.

Formaldehyde in Atmospheric Air. H. HENRIET (*Compt. rend.* 1904, 138, 203—205. Compare Abstr., 1902, i, 714; 1903, i, 600).—On distilling the liquid obtained by evaporating to 200 c.c. 30 to 40 litres of condensed atmospheric moisture, the distillate contains in addition to formic acid an aldehyde which reduces Nessler's reagent, ammoniacal silver nitrate, and Fehling's solution, and gives a reddish-violet coloration with a solution of magenta decolorised by sulphurous acid. This aldehyde is identified with formaldehyde by the following specific reactions: (1) Lebbin's reaction, the formation of a red coloration on boiling the aldehydic solution with an alkaline solution of resorcinol. (2) Farnsteiner's reaction, the development of a rich violet colour with a dilute solution of peptone, sulphuric acid, and ferric chloride; this reaction, which is a very delicate test for formaldehyde, is also given by the liquid obtained by bubbling filtered air through distilled water. (3) The formation of hydrogen cyanide by distilling with sulphuric acid the product of the action of hydroxylamine hydrochloride on an alkaline solution of the liquid. (4) The formation of the blue colour of tetramethyldiaminobenzhydrol (Michler's hydrol), by oxidising the product obtained by boiling the aldehydic liquid with dimethylaniline and sulphuric acid.

The quantity of formaldehyde in the air varies from 1 to 5 parts per 100,000, and is proportional to the temperature.
M. A. W.

Oxidation of Formaldehyde by Peroxides. HANS GEISOW (*Ber.*, 1904, 37, 515—520).—When formaldehyde is oxidised by hydrogen peroxide in neutral or acid solution, hydrogen is evolved, but no formic acid could be detected. The action proceeds thus: $\text{CH}_2\text{O} + \text{H}_2\text{O}_2 = \text{CO}_2 + \text{H}_2\text{O} + \text{H}_2$. In order to establish whether the hydrogen evolved had its origin from the formaldehyde used, experiments were made with barium peroxide and formaldehyde, when it was found that hydrogen was also evolved and that the barium peroxide was converted into carbonate. When the experiment was conducted with a dilute solution of formaldehyde and the temperature kept below the boiling point of water, no formate was obtained, but only carbonate.

The action of manganese peroxide and lead peroxide respectively

on formaldehyde led to the formation of the corresponding formates ; neither carbon dioxide nor carbonate could be detected in either case.

A. McK.

Preparation of Acetone. L. WENGHÖFFER (D.R.-P. 144328).—A metallic acetate, in the form of a solution or in a pasty condition, is gradually introduced into a heated vessel. The moist mass is so rapidly decomposed that acetone and water-vapour pass off together, and local charring is avoided.

C. H. D.

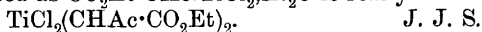
Alkyl Allyl Ketones. EDMOND E. BLAISE (*Compt. rend.*, 1904, 138, 284—286).—With the view of extending his investigation on the acid nature of the hydrogen atoms of a methylene group situated between a carbonyl radicle and an ethylenic carbon atom (compare Abstr., 1903, i, 400, 549), the author has prepared a series of alkyl allyl ketones of the type $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{COR}$ by the condensation of allyl iodide with a fatty nitrile in benzene solution in the presence of zinc at a temperature of 0° , and the subsequent decomposition of the initial additive product by dilute sulphuric acid, according to the following equations: $\text{CH}_2\text{:CH}\cdot\text{CH}_2\text{I} + \text{RCN} + \text{Zn} = \text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CR:N}\cdot\text{ZnI}$; $2\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CR:N}\cdot\text{ZnI} + 4\text{H}_2\text{O} = 2\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{COR} + 2\text{NH}_3 + \text{ZnOH} + \text{ZnI}_2$. The ketones are colourless, mobile liquids, boiling without alteration under atmospheric pressure, and there is a difference of about 20° between the boiling points of two consecutive homologues; they have agreeable odours, readily form semicarbazones and liquid oximes which boil in a vacuum without alteration. Owing to their unsaturated character, they are readily oxidised by permanganate solution in the cold, and unite directly with the halogen acids with development of heat; the saturated brominated ketones obtained by the union of the alkyl allyl ketone with hydrogen bromide are very unstable, although they can be distilled in a vacuum without undergoing decomposition. The bromine in these compounds is in the β -position; on boiling with an alkali solution or even with water only, they lose hydrogen bromide, yielding the propenyl ketone isomeric with the original: $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{COR} \rightarrow \text{CH}_3\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{COR} \rightarrow \text{CH}_3\cdot\text{CH:CH}\cdot\text{COR}$. These propenyl ketones, also formed in small quantity in the preparation of the allyl ketones, boil about 10° lower than the isomeric allyl compound and readily form semicarbazones.

M. A. W.

Action of Titanium Tetrachloride on 1:3-Diketones. WALTHER DILTHEY (*Ber.*, 1904, 37, 588—592).—The products described by Rosenheim, Loewenstamm and Singer (Abstr., 1903, i, 603) are similarly constituted to the silicon derivatives previously prepared by the author (*ibid.*, 405, 591, and this vol., i, 132). The compound described as $\text{TiCl}_3\cdot\text{CHAc}_2\cdot\text{Et}_2\text{O}$ is really $\text{TiCl}_2(\text{CHAc}_2)_2$, and may also be obtained from chloroform solutions. It may be crystallised from a small amount of glacial acetic acid, and appears to be termolecular. It forms a compound with ferric chloride, having the composition $\text{TiFeCl}_4(\text{CHAc}_2)_3$, and crystallising in reddish-yellow needles. The

platinichloride, $[\text{Ti}(\text{CHAc}_2)_3]_2\text{PtCl}_6$, crystallises in brownish-yellow prisms.

The compound described as $\text{CO}_2\text{Et}\cdot\text{CAC}\cdot\text{TiCl}_2\cdot\text{Et}_2\text{O}$ is really



Action of Dilute Sulphuric Acid on Butyronepinacone. KARL ZUMPF (Monatsh., 1904, 25, 124—134).—On heating butyronepinacone with 20 per cent. sulphuric acid in a sealed tube for 7 hours at 150° and then for 5 hours at 170 — 180° , a mixture is formed which contains principally the two following products:

(1) A *hydrocarbon*, $\text{C}_{14}\text{H}_{26}$, which is a colourless, oily liquid with a faint aromatic odour, and boils at 216 — 218° under the ordinary pressure, and at 98 — 100° under 13 mm. pressure; it is readily soluble in alcohol or ether, and yields a *dibromide*, $\text{C}_{14}\text{H}_{26}\text{Br}_2$, separating from carbon disulphide in scales melting at 83° ; on oxidation with chromic acid, it gives acetic, propionic, and butyric acids.

(2) An *oxide*, $\text{C}_{14}\text{H}_{28}\text{O}$, which is a yellow, oily liquid with an empyreumatic smell and a bitter taste; it boils at 243 — 244° under the ordinary pressure, and at 122 — 124° under 13 mm., and on oxidation with chromic acid or permanganate yields only a trace of fatty acids; it does not give an oxime, acetyl derivative, or phenylhydrazone, and does not react with zinc ethyl or with water or aqueous alcohol in a sealed tube, and hence is probably a 1:4- or 1:5-oxide.

With boric acid also, butyronepinacone yields a mixture of the above hydrocarbon and oxide. T. H. P.

New Bases derived from Sugars. II. E. Roux (*Ann. Chim. Phys.*, 1904, [viii], 1, 160—185).—The preparation, properties, and derivatives of arabinamine and of xylamine described in this paper have already been published (compare Abstr., 1903, i, 463). Arabinamine hydriodide melts without decomposition at 190 — 191° , and the picrate decomposes at 144 — 145° . Xylamine hydriodide melts without alteration at 206° , and has $[\alpha]_D - 12.50^\circ$; the hydrochloride crystallises in deliquescent, prismatic needles, and is soluble in ethyl or methyl alcohol. M. A. W.

Mannamine, a New Base Derived from Mannose. E. Roux (*Compt. rend.*, 1904, 133, 503—505. Compare Maquenne and Roux, Abstr., 1901, i, 372; 1902, i, 266, 696; 1903, i, 73, 463).—Mannamine, prepared by reducing mannoseoxime, is identical with the base formed together with glucamine when *isoglucosamine* is reduced by sodium amalgam (compare Maquenne, this vol., i, 18), and forms a partially crystalline mass very soluble in water or alcohol, which melts at about 139° , has a caustic but sweet taste, has $[\alpha]_D - 2^\circ$ in 10 per cent. aqueous solution, and shows no multirotation. It forms a precipitate with nickel sulphate, and gives a white, amorphous product with mercuric chloride, insoluble in excess of the base. The *oxalate*, $(\text{C}_6\text{H}_{15}\text{O}_5\text{N})_2\cdot\text{C}_2\text{O}_4\text{H}_2$, forms brilliant, lozenge-shaped plates, melts at 186° , has $[\alpha]_D + 4.25^\circ$ in 10 per cent. aqueous solution, is very soluble in water, but insoluble in alcohol, and loses 1 mol. of water on being heated for some time just above its melting point, forming *dimann-*

oxamide, $C_2O_2(NH \cdot C_6H_{13}O_5)_2$, which crystallises in thin, hexagonal plates melting at $218-219^\circ$, and is soluble in alcohol or water.

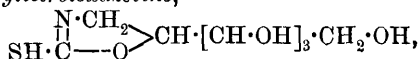
The *sulphate* and *hydrochloride* are crystalline and soluble in water, but insoluble in alcohol. The *platinichloride* crystallises in yellow, prismatic needles, and is slightly soluble in alcohol.

Mannamininecarbamide, $C_6H_{13}O_5 \cdot NH \cdot CO \cdot NH_2$, prepared from potassium cyanate and mannamine sulphate, crystallises in tufts of slender, prismatic needles, melts at $97-98^\circ$, is readily soluble in water, but less so in alcohol. The *phenylcarbamide*, $C_6H_{13}O_5 \cdot NH \cdot CO \cdot NHPh$, produced by the action of phenylcarbamide on mannamine in pyridine solution, crystallises in elongated, trapezoidal plates, which melt at 202° and are slightly soluble in alcohol or water.

Acetylacetonemannamine, $CH_2Ac \cdot CMe \cdot N \cdot C_6H_{13}O_5$, obtained by the action of boiling acetylacetone on mannamine, forms thin, long needles, melts at 172° , is readily soluble in water or alcohol, and rapidly hydrolysed by dilute acids.

Benzylidenemannamine, $C_6H_{13}O_5 \cdot N : CHPh$, produced by the condensation of benzaldehyde and mannamine, forms small crystals, decomposes at 183° , is slightly soluble in alcohol, and readily decomposed by cold water.

2-Thiol-5-butyltetrolloxazoline,



prepared by the action of carbon disulphide on mannamine, forms small, prismatic crystals, melts at 216° , is soluble in boiling water, slightly so in alcohol, and gives a crystalline derivative with silver nitrate.

M. A. W.

Phenomena of Rotation of Lactose. HEINRICH TREY (*Zeit. physikal. Chem.*, 1903, 46, 620—719. Compare Abstr., 1896, ii, 139; 1897, ii, 299; also Hudson, Abstr., 1903, ii, 623).—The decrease in the rotation of lactose hydrate and the increase in that of lactose anhydride are changes which follow the same course as a reaction of the first order, and are represented by the formula $C = 1/t \cdot \log A/(A - x)$. The velocity of the change of rotation for the hydrate is ten times greater at 25° than at 0° , for the anhydride eight times greater. Addition of methyl or ethyl alcohol retards both changes, and the retardation is nearly proportional to the amount of alcohol added. A similar remark applies to aqueous acetone solutions of lactose hydrate and anhydride. Both the decrease of rotation of lactose hydrate and the increase of rotation of lactose anhydride are accelerated by acids, and experiments at 0° have shown that the acceleration produced by an acid depends on its affinity constant. Sodium hydroxide and ammonia, when present in fair quantity, give at once the same rotation value in both hydrate and anhydride solutions, and this is followed by a slow decrease in both cases. In very dilute solutions, sodium hydroxide and ammonia do not at once produce the same rotation value, but accelerate the change of rotation of the hydrate and of the anhydride as indicated above in the case of acids. This accelerating effect is intensified by the addition of alcohol. Sodium carbonate and triammonium phosphate in $N/10$ solution also produce immediately

the constant rotation value of lactose hydrate. The effect of many other substances has been tested, for example, sodium hydrogen carbonate, borax, sodium tungstate, ammonium molybdate, carbamide, and neutral salts, such as barium chloride, magnesium sulphate, potassium iodide, and ammonium chloride. These substances accelerate the change of rotation both of the hydrate and of the anhydride. Sodium chloride is without effect.

The author attributes the changes of rotation described above to changes of configuration that take place gradually in solution.

J. C. P.

The Inversion of Sugar. LÉON LINDET (*Compt. rend.*, 1904, 138, 508—510).—The author has measured the electrolytic conductivity of 10 per cent. aqueous solutions of sugars which have been boiled for 4 hours, and finds that if the conductivity of distilled water is taken as unity, that of sucrose is 1.3, that of *lævulose* 3.7, and that of dextrose 5.1; the conductivity of sucrose is increased by the addition of 1/3000 of inverted sugar, and the different commercial raffinoses have a conductivity varying with the amount of dextrose they contain (compare Prinsen Geerligs, *Abstr.*, 1899, i, 101; Kullgren, *Abstr.*, 1901, ii, 149; 1902, ii, 647). Rayman and Šulc (compare *Abstr.*, 1896, i, 459; 1897, ii, 136; 1898, i, 348; 1899, i, 102) have shown that sucrose is not inverted when heated with water in glass vessels, whilst in some metallic vessels the inversion proceeds rapidly; the author shows that the retarding influence of glass is to be attributed to the extraction by the water of alkali silicates, which neutralise the acid produced during the inversion and so check the process. The effect of metals in the form of powder or turnings on the inversion of sugar has also been examined, and it is found that copper, lead, tin, and bismuth are very active in this respect; aluminium and antimony are less so, whilst nickel, chromium, arsenic, gold, platinum, silver, and mercury are indifferent, and cobalt, iron, zinc, cadmium, and magnesium have a retarding influence. It is suggested that the hydroxide of the metal is formed by the action of the air and water, and this has an accelerating or retarding effect according as it is of an acidic or basic character, whilst those metals which are inert are also those which do not yield hydroxides under the conditions of the experiment.

M. A. W.

A Labile Nitrate of Cellulose. EDMUND KNECHT (*Ber.*, 1904, 37, 549—552).—When cellulose is soaked in nitric acid of sp. gr. 1.415, it takes up 36 per cent. of HNO_3 , forming a compound $\text{C}_6\text{H}_{10}\text{O}_5\cdot\text{HNO}_3$ (this requires 37.2 per cent. HNO_3), which is decomposed by water. The excess of acid cannot be removed satisfactorily by washing, but is got rid of by exposure in a desiccator over freshly burnt lime. The product obtained by the action of water contains 4 per cent. more water than normal cellulose and is probably a hydrate. Heating in a vacuum at 100° causes the liberation of nitrous fumes, and leaves a product, insoluble in sodium hydroxide and capable of reducing Fehling's solution, which appears to be identical with Cross and Bevan's oxycellulose. The process is closely

analogous to that involved in mercerisation, in which the cellulose forms an additive compound, $C_6H_{10}O_5 \cdot Na_2O$, in which (on washing with water) the soda is replaced by water forming a hydrate; after treatment with nitric acid and water, the cellulose fibres were found to have shrunk 13 per cent. and to have increased greatly in tensile strength.

T. M. L.

Formation and Saccharification of Reverted Starch. LÉON MAQUENNE (*Compt. rend.*, 1904, 138, 213—214. Compare Abstr., 1903, i, 679; this vol., i, 17, 227).—In the experiments hitherto made on the reversion (transformation) of starch paste, fairly concentrated solutions of the paste have been used; it is now found that the extent of the reversion, as measured by the amount of amylocellulose formed, increases with the concentration of the starch paste, at first rapidly, but afterwards more slowly. The amylocellulose formed by the reversion of starch paste is partly rendered soluble by amylase if the saccharification is conducted at a sufficiently high temperature, but it never becomes entirely soluble, even after being heated anew to 130° . It is probable that amylocellulose is not a definite compound, but a mixture of several different condensation products which have the property in common of not being coloured by iodine, and the distinctive characteristics of offering specific resistances to the solvent action of amylase.

M. A. W.

Nature of Raw Starch. LÉON MAQUENNE (*Compt. rend.*, 1904, 138, 375—377. Compare Abstr., 1903, i, 675; this vol., i, 17).—The paste freshly prepared from raw starch is rendered completely soluble by amylase or by mineral acids; only 2.8 per cent. of the raw starch grains becomes soluble under similar treatment, whilst 94.8 per cent. becomes soluble if the grains have been previously pulverised, thus, as Brown and Héron have shown, the effect of mechanically destroying the protecting envelope of the grains is almost the same as that produced by converting it into a jelly. From a chemical point of view, therefore, the starch grain possesses the same composition as starch paste which has been prepared some time, that is, it is *reverted starch*, a mixture of amylocelluloses in various states of condensation. It is because these amylocelluloses redissolve at a high temperature that they are not present in freshly prepared starch paste, and because they are formed from pure starch in the cold that they are present in raw starch grains and reverted starch.

M. A. W.

Composition of Potato-starch. AUGUSTE FERNBACH (*Compt. rend.*, 1904, 138, 428—430).—When potato-starch is levigated, two kinds of granules, the heavy and the light, are obtained. Both of these contain phosphorus, and analysis shows that the light granules contain a greater percentage of that element than the heavy grains. In six samples examined, the heavy granules contained 138—178 mg. P_2O_5 , and the lighter granules 158—226 mg. P_2O_5 per 100 grams.

S. S.

Pure Glycogen. MADAME Z. GATIN-GRUZEWSKA (*Pflüger's Archiv*, 1903, 100, 634—635).—Pure glycogen, obtained by Pflüger's method and quite free from nitrogen, when precipitated by alcohol from an aqueous solution, comes down in the shape of clumps and rods, with forms intermediate between them. In some cases, the rods are quite long. This character is recommended as a criterion of the purity of glycogen. W. D. H.

Electrolytic Preparation of Fatty Amines. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 148054).—The products of condensation of aldehydes with ammonia may be conveniently reduced by electrolysis in neutral or ammoniacal solution. Thus a solution of hexamethylenetetramine and sodium sulphate may be electrolysed between lead electrodes, employing a current-density of 3 amperes per sq. dm., and a potential difference of 3.5 volts, sulphuric acid being added from time to time in the neighbourhood of the cathode to maintain neutrality. In place of the condensation products, a mixture of the aldehyde with ammonia or ammonium salts may be electrolysed directly. C. H. D.

[Electrolytic] Preparation of Nitro- and Amino-compounds. MORITZ LILIENFELD (D.R.-P. 147943).—In the removal of the carboxyl group from fatty or aromatic carboxylic acids by electrolysis, the copper salts may advantageously be employed in place of the alkali salts. The evolution of gas at the electrodes is thus avoided, as well as the formation of an alkali hydroxide, which may give rise to secondary reactions. The conductivity of the copper salts is also greater than that of the alkali salts, and the end of the reaction is easily determined by the disappearance of the blue colour. Thus a solution of copper glycine, electrolysed with a current-density of 0.1 ampere per 1000 sq. mm., and a tension of 1.75 volts, yields ethylenediamine, $\text{Cu}(\text{CO}_2 \cdot \text{CH}_2 \cdot \text{NH}_2)_2 = \text{Cu} + 2\text{CO}_2 + \text{C}_2\text{H}_4(\text{NH}_2)_2$. The preparation of benzidine from copper *p*-aminobenzoate, and that of *p*-dinitrodiphenyl from copper *p*-nitrobenzoate, are also described. When nitro-acids are employed, the electrolysis may be continued until the nitro-group has been reduced to the amino-group. The salts of other heavy metals may be employed in place of copper salts, but with less advantage.

C. H. D.

Preparation of Aminoaldehydes. CARL D. HARRIES and PAUL REICHARD (*Ber.*, 1904, 37, 612—615).—An aqueous solution of allylamine hydrochloride is readily oxidised by ozone to aminoacetaldehyde hydrochloride, hydrogen peroxide being formed at the same time.

The *platinichloride*, $[\text{CHO} \cdot \text{CH}_2 \cdot \text{NH}_2]_2, \text{H}_2\text{PtCl}_6$, crystallises in pale yellow plates melting and decomposing at 185°, and is quite different from the platinichloride described by E. Fischer (*Abstr.*, 1893, i, 187, 300). Fischer's aminoacetaldehyde also yields a platinichloride free from alcohol, but this melts at 125°, does not decompose at 185°, and is less soluble in water. It is suggested that the aminoacetaldehyde obtained by Fischer may be the hydroxymethylene compound

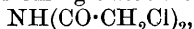
$\text{NH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{OH}$, whereas the product from allylamine hydrochloride has the aldehydic structure $\text{NH}_2\cdot\text{CH}_2\cdot\text{CHO}$; α -aminopropaldehyde hydrochloride may be obtained by a similar process. J. J. S.

Preparation of Formiminoethyl Ether. HENRY B. HILL and O. F. BLACK (*Amer. Chem. J.*, 1904, 31, 207—209).—When dry hydrogen chloride is passed into a mixture of mercuric cyanide (1 mol.), mercuric chloride (1 mol.), and ethyl alcohol (2 mols.) diluted with several times its volume of ether at 0° , the *mercury* double salt of formiminoethyl ether hydrochloride, $\text{NH}\cdot\text{CH}\cdot\text{OEt}\cdot\text{HCl}\cdot\text{HgCl}_2$, separates in colourless plates. This compound is comparatively stable and, when heated with aniline, yields diphenylformamidine. It reacts with alcohol with formation of ethyl orthoformate, and can, therefore, be used in place of formiminoethyl ether hydrochloride in the preparation of acetals by Claisen's method.

Zinc cyanide yields a similar double salt of formiminoethyl ether hydrochloride which is deliquescent, but silver and potassium cyanides do not furnish compounds of this kind. E. G.

Action of Nitriles on Carboxylic Acids. W. KÖNIG (*J. pr. Chem.*, 1904, [ii], 69, 1—39).—Nitriles react with carboxylic acids to form secondary amides, except in the case of a fatty nitrile and an aromatic acid, when exchange of the cyano- and carboxy-groups takes place (Colby and Dodge, *Abstr.*, 1891, 409). The entrance of negative groups into the molecule should facilitate the reaction, and this is found to be the case.

Chloroacetonitrile and chloroacetic acid react together when heated three hours at $135\text{--}140^\circ$, forming *s-dichlorodiacetamide*,

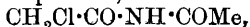


which crystallises from acetone in silvery-white leaflets, and melts and decomposes at 189° . The dust violently attacks the mucous membrane. It is insoluble in ether, sparingly soluble in benzene, chloroform, or light petroleum, readily so in hot water, alcohol, acetone, or acetic acid. Alkalis hydrolyse it, and prolonged boiling with alcohol forms ethyl chloroacetate and chloroacetamide. Chloroacetonitrile and dichloroacetic acid react at 130° to form *chloroacetyldichloroacetamide*,



crystallising from a mixture of benzene and light petroleum in star-shaped groups of needles and melting at 98° . Chloroacetonitrile and trichloroacetic acid react at 120° to form *chloroacetyltrichloroacetamide*, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CCl}_3$, crystallising from light petroleum in leaflets and melting at 80° , dissolving readily in most solvents and deliquescing in moist air, at the same time undergoing partial hydrolysis. *Chlorobromodiacetamide*, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Br}$, from chloroacetonitrile and bromoacetic acid at 110° , crystallises from benzene in pearly leaflets and melts and decomposes at 180° .

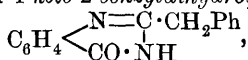
The symmetrical structure of the secondary amides is proved by the fact that chloroacetonitrile and acetic acid, or acetonitrile and chloroacetic acid, yield the same product, *chlorodiacetamide*,



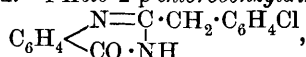
crystallising from benzene in pearly leaflets and melting at 105—106°. In similar manner, *p*-chlorophenylacetonitrile and phenylacetic acid, or phenylacetonitrile and *p*-chlorophenylacetic acid, form *p*-chlorodiphenyl-diacetamide, $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\text{Cl}$, crystallising from alcohol in white needles and melting at 172°, dissolving sparingly in water, ether, or light petroleum, readily in hot benzene or alcohol.

Succinic acid reacts with succinonitrile at 260°, forming succinimide, probably owing to decomposition of the unstable secondary amide at first formed. No amides were obtained from acetonitrile and trichloroacetic acid, acetonitrile, benzonitrile, or phenylacetonitrile and thioacetic acid, benzoyl cyanide and phenylacetic acid, or from chloroacetonitrile and mandelic acid. Cyanogen bromide and bromo- or cyanoacetic acid also gave no definite reaction.

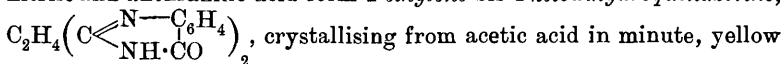
Nitriles condense with *ortho*-substituted aromatic acids, forming quinazoline derivatives. Secondary amides are probably formed in the first place, and water is then eliminated. Anthranilic acid and phenylacetonitrile at 145° form 4-*keto*-2-benzylidihydroquinazoline,



which crystallises from acetic acid in silky, felted needles, melts at 242°, and is insoluble in water, but very soluble in pyridine. Warm solutions of alkali hydroxides dissolve it, forming salts, but no salt with hydrochloric acid could be obtained. 4-*Keto*-2-*p*-chlorobenzylidihydroquinazoline,



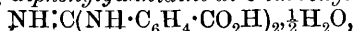
from anthranilic acid and *p*-chlorophenylacetonitrile, softens at 240° and melts and decomposes at 246°. Benzoyl chloride in pyridine solution forms 4-*keto*-2-*p*-chlorobenzyl-3-benzoyldihydroquinazoline, which forms white, felted needles, sinters at 170°, and melts at 210°. Succinonitrile and anthranilic acid form 2-ethylene-bis-4-*keto*dihydroquinazoline,



crystallising from acetic acid in minute, yellow needles, very sparingly soluble in all solvents except pyridine, and melting above 310°. Boiling with dilute acetic acid causes it to take up H_2O , which is only lost at 190—200°. It has both acid and basic properties, forming crystalline *sodium*, *copper*, *silver*, and *ferric* salts, and a *platinichloride* $\text{C}_{18}\text{H}_{16}\text{O}_2\text{N}_4\text{PtCl}_6$ in yellow needles, decomposing above 300°. Anthranilic acid and cyanoacetic acid form cyanoacetanilide; anthranilic acid and benzoyl cyanide form benzoylanthranilic acid. Phthalimide and anthranilic acid form a *compound*, $\text{C}_{21}\text{H}_{14}\text{O}_3\text{N}_2$, crystallising from alcohol in white needles, very sparingly soluble in water, readily in alcohol or acetic acid. This is not, as might be expected, *o*-phthaliminobenzanilide, since this, prepared synthetically from phenyl-*o*-aminobenzamide and phthalic anhydride, was found to melt at 205°.

Salicylic acid and phenylacetonitrile form phenylacetamide and a salicylide.

Cyanogen bromide reacts with a hot aqueous solution of anthranilic acid, forming *diphenylguanidine-di-o-carboxylic acid*,



which crystallises from acetic acid in small, greenish-yellow needles, very sparingly soluble in most solvents, and melting and decomposing at 201° . The metallic salts are crystalline and characteristic. The constitution was established by conversion into 2:4-diketotetrahydroquinazoline and anthranilic acid by boiling with alkalis or acids, and by conversion into 3:4-dibromoanthranilic acid by bromine. Anthranilamide and cyanogen bromide form *diphenylguanidine-di-o-carboxylamide*, $\text{NH}\cdot\text{C}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CONH}_2)_2\cdot\text{H}_2\text{O}$, crystallising from water in star-shaped groups of needles and melting above 290° , sparingly soluble in most solvents, readily so in glacial acetic acid to a solution with blue fluorescence. Acids or alkalis yield the same products as in the case of the carboxylic acid. The amide forms an orange, crystalline *chromate*, and a *picrate*, $\text{C}_{15}\text{H}_{15}\text{O}_2\text{N}_5\cdot\text{C}_6\text{H}_8\text{O}_7\text{N}_3$, crystallising from nitrobenzene in yellow, concentrically grouped needles with green fluorescence, and melting above 280° .

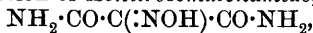
Mono- and di-bromo- and nitro-anthranilic acids do not react with cyanogen bromide. C. H. D.

Action of Nitrous Acid on the Amide of Malonic Acid and its Homologues. FLORIAN RATZ (*Monatsh.*, 1904, 25, 55—123).—The action of fuming nitric acid of sp. gr. 1.47—1.50 on an aqueous solution of malonamide yields nitromalonamide, $\text{C}_3\text{H}_5\text{O}_4\text{N}_3$ (see Riche-mann and Orton, *Trans.*, 1895, 67, 1002), which is also obtained by the action of boiled nitric acid on the amide suspended in sulphuric acid, and by the addition of aqueous sodium nitrite to a cold solution of the hydrochloride of the amide; concentrated nitric acid, quite free from nitrous acid, is without action on the amide. Nitromalonamide has strongly acid properties, decomposing carbonates and forming characteristic monobasic salts; the silver salt is white, and not yellow as has been stated. The action of an alkyl iodide on the silver salt yields not a substituted derivative of nitromalonamide, but the latter itself.

In order to compare the various compounds obtained with respect to their power of yielding ammonia when treated with acids or alkalis, the author has used the method of distillation in a current of steam, the amount of ammonia in the distillate being determined from time to time. When acids are used, the substance and acid are heated together for a certain time by means of a current of steam, excess of alkali being then added and the ammonia distilled off in a current of steam; in this case, the effect of the alkali added must be subtracted.

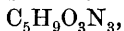
With dilute sulphuric acid, nitromalonamide readily yields 2 mols. of ammonia, but with potassium hydroxide only 1 atom of nitrogen is eliminated readily and the other much more slowly. Water exerts a hydrolysing action on nitromalonamide, yielding the ammonium derivative; besides this, a further action takes place giving rise to:

(1) A small proportion of *isonitrosomalonicamide*,



which separates from 70 per cent. aqueous alcohol in pale yellow needles melting and decomposing at about 175.5° ; it is readily soluble in water, ethyl or methyl alcohol, or acetone, and slightly so in ether,

benzene, or chloroform, and has the normal molecular weight in aqueous solution. It yields a *silver* derivative, $C_3H_4O_3N_3Ag$, separating in concentrically-arranged, greenish-yellow needles, a white, amorphous *lead* compound, and a green, crystalline, *copper* derivative. When hydrolysed with dilute acids, it yields two of its nitrogen atoms in the form of ammonia and the third as hydrogen cyanide, whilst with alkalis it yields only 2 mols. of ammonia. When its aqueous solution is left in contact with metallic iron, best powdered, it assumes an intense bluish-violet colour; this reaction is also given with zinc dust and a ferrous salt, or with sodium acetate and a ferrous salt, excess of the latter causing its disappearance. This colour is also destroyed by traces of an acid or alkali, and may hence serve as a very sensitive indicator. The *methyl* derivative, $C_4H_7O_3N_3$, separates from alcohol in needles melting at 143.5 — 144.5° , and is readily soluble in water or methyl alcohol; when hydrolysed by means of alkalis, it gives up 2 atoms of nitrogen very readily as ammonia, whilst with acids it yields also a third nitrogen atom as hydrogen cyanide; it gives a slight coloration with ferrous salts, but this is probably due to the presence of small quantities of the parent substance. The *ethyl* derivative,

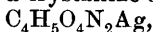


separates from aqueous solution in crystals melting at 150.5 — 151.5° ; it gives no coloration with ferrous salts. The constitution of *isonitrosomal*onamide was confirmed by synthesising it as follows: ethyl nitrosomalonate was prepared by passing nitrogen trioxide (from arsenious anhydride and nitric acid) into an absolute alcoholic solution of ethyl sodiomalonate until a neutral reaction is obtained; if the gas is passed slowly into the ice-cold solution, yields of 90—95 per cent. can be obtained (see Conrad and Bischoff, Abstr., 1880, 629). The action of alcoholic ammonia on ethyl nitrosomalonate yields the ammonium derivative of *isonitrosomal*onamide, which, with silver nitrate, gives the silver derivative of *isonitrosomal*onamide.

Hydrolysis of *isonitrosomal*onamide with dilute sulphuric acid yields two isomeric compounds, $C_3H_4O_4N_2$, which both act as dibasic acids, one hydrogen atom being very strongly acidic in character and the other much less so. Both contain a nitrogen atom capable of yielding ammonia very readily on treatment with acids and less readily with alkalis; the second nitrogen atom is given up in the form of hydrogen cyanide. Both form crystals decomposing at about 139 — 140° . The two compounds (α - and β -) differ widely in their solubilities in alcohol, and also exhibit differences in their velocities of hydrolysis by means of acid or alkali. Neither alone nor in presence of 1 mol. of sodium hydroxide do these compounds give any characteristic reaction with ferrous salts, but if a little sodium acetate or another mol. of sodium hydroxide is added, an intense violet coloration (in presence of $\frac{1}{2}$ mol. of ferrous sulphate) or a dark blue precipitate (with 1 mol. of ferrous sulphate) is obtained; these dark blue ferrous compounds are not formed if even traces of acid are present, but, when once formed, are very stable, and are not destroyed either by heating or by the addition of a concentrated acid or alkali solution. Both the α - and β -compounds form silver derivatives, $C_3H_3O_4N_2Ag$ and $C_3H_2O_4N_2Ag_2$, and also mono-

methyl compounds. The nature of their isomerism has not been definitely settled, but it is supposed that they are *anti*- and *syn*-forms.

On hydrolysing the methyl derivative of isonitrosomalonomide so as to remove one amino-group, a compound, $C_4H_6O_4N_2$, is obtained, which separates from alcohol, or a mixture of alcohol and chloroform, in microscopic rhombohedra melting and decomposing at $137-138^\circ$; it is a monobasic acid, and yields a crystalline *silver* compound,



and readily soluble *copper* and *lead* derivatives. When both the amino-groups of the methyl derivative of isonitrosomalonomide are removed by hydrolysis, a dibasic acid, $C_4H_5O_5N$, is obtained, which crystallises from benzene in a felted mass of slender needles, melting without decomposing at $90-91^\circ$; it is readily soluble in water, methyl or ethyl alcohol, acetone, or ether, and yields an insoluble *lead* salt and a crystalline *silver* salt, $C_4H_3O_5NAg_2 \cdot \frac{1}{2}H_2O$; it is identical with the compound obtained by methylating isonitrosomalonic acid.

On oxidising isonitrosomalonomide with acid permanganate, it yields nitromalonamide.

(2) The second product of the action of water on nitromalonamide proved to be a mixture of at least two compounds. The first of these is a *polyamide*, $(C_6H_9O_5N_6)_n$, which separates from aqueous alcohol in yellowish-red crystals, but was not obtained quite free from ash (about 0.3 per cent.); when hydrolysed with acid or alkali, it gives up three-fourths of its nitrogen in the form of ammonia, so that the empirical formula must at least be doubled; on restricted hydrolysis, it yields an acid giving a *silver* salt of the composition $(C_6HO_5N_2Ag_4)_n$. Another compound, obtained from this mixture, separates from water in microscopic, club-shaped, and drusy, crystalline masses having the composition $(C_6H_{11}O_6N_6)_n$.

(3) Another compound separated from the solution obtained by the action of water on nitromalonamide is slightly soluble in water, acetone, methyl or ethyl alcohol, and gives a *silver* derivative, $(C_3H_2O_3N_2Ag)_n$, which was not obtained in a pure state [compare M. A. Whiteley, *Trans.*, 1903, 83, 24].

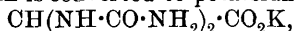
T. H. P.

The Diureides. Ethyl Homoallantoate. LOUIS J. SIMON (*Compt. rend.*, 1904, 138, 372-374).—Ethyl homoallantoate (compare *Abstr.*, 1902, i, 15), prepared by the direct action of carbamide on ethyl pyruvate, is a white, microcrystalline solid, decomposing at about 200° , insoluble in cold water or most organic solvents, slightly soluble in boiling alcohol, and more so in the presence of pyridine; it is hydrolysed by the action of boiling water into carbamide and ethyl pyruvate, and decomposed by concentrated hydrochloric acid into pyruvic acid and dipyruvyltriureide (compare *Abstr.*, 1903, i, 314); it is slightly soluble in concentrated solutions of ammonia or methylamine, and from the solutions, crystals of homoallantoin (pyruvil) slowly separate; alcoholic or aqueous solutions of potassium carbonate effect a similar change, the potassium derivative of homoallantoin being produced, which is insoluble in the alcoholic, but soluble in the aqueous solution, and readily converted into homoallantoin by hydrochloric acid.

M. A. W.

Ureides of Glyoxylic Acid: Allantoin and Allantoic Acid.
 LOUIS J. SIMON (*Compt. rend.*, 1904, 138, 425—428).—Allantoin dissolves in strong aqueous potassium hydroxide, giving a clear solution which, after a short time, deposits a thick, crystalline precipitate of potassium allantoin, $\text{CO} \begin{smallmatrix} \text{NK} \cdot \text{CO} \\ | \\ \text{NH} \cdot \text{CH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2 \end{smallmatrix}$.

After the lapse of a few hours, a further change takes place, and the potassium allantoin is converted to potassium allantoate,



which is crystalline, and soluble in water. Allantoic acid can be obtained from this salt as a white, crystalline powder, which decomposes when heated at about 165°. It is very slightly soluble in water, dilute acids, and organic solvents, but dissolves in potassium carbonate solutions, liberating carbon dioxide; it is also soluble in solutions of potassium acetate. Silver allantoate is insoluble in water. Allantoic acid is decomposed by warm water, dissolving therein and giving carbamide and glyoxylic acid; the same decomposition may take place in cold acidified solutions of the potassium salt. If the solution of allantoic acid is heated for a longer period, a certain amount of allantoin is formed. S. S.

Some Compounds of Cuproso-cupric Cyanide with Pyridine, Methylamine, Dimethylamine, and Trimethylamine.
 FRANZ M. LITERSCHIED (*Arch. Pharm.*, 1904, 242, 37—42. Compare Schmidt and Malmberg, *Abstr.*, 1898, i, 547).—A reddish-brown precipitate of the composition $\text{Cu}_3(\text{CN})_4, 5\text{C}_5\text{H}_5\text{N}$ is obtained by adding pyridine to aqueous copper sulphate until the precipitate that forms at first has redissolved, and then adding aqueous potassium cyanide cautiously. Shaking with much water converts it into a green compound, $\text{Cu}_3(\text{CN})_4, 3\text{C}_5\text{H}_5\text{N}$; heating for 24—30 hours at 100° into a yellowish-brown compound, $\text{Cu}_3(\text{CN})_4, 2\text{C}_5\text{H}_5\text{N}$, whilst prolonged heating at 105—110° drives off all the pyridine from it (exposure to the air for days also effects this).

A green precipitate or green crystals, having the composition $\text{Cu}_3(\text{CN})_4, 4\text{NH}_2\text{Me}$,

are obtained by adding aqueous potassium cyanide to aqueous copper sulphate until the precipitate that forms at first has redissolved, and then adding methylamine. Similar green amorphous compounds, $\text{Cu}_3(\text{CN})_4, 4\text{NHMe}_2$ and $\text{Cu}_3(\text{CN})_4, 4\text{NMe}_3$, are obtained by using di- and tri-methylamines instead of methylamine. In all three cases, blue compounds containing more than 4 mols. of the base were prepared, but they had no definite composition. C. F. B.

Hydrargyrum Oxycyanatum. E. HOLDERMANN (*Arch. Pharm.*, 1904, 242, 32—36).—Aqueous mercuric cyanide, suitably about 13 per cent. in strength, dissolves freshly precipitated mercuric oxide, when digested with this on the water-bath in proportions corresponding with the formula $3\text{Hg}(\text{CN})_2, \text{HgO}$, and the crystals which separate when the filtered solution is concentrated have a corresponding composition. No compound in other proportions could be obtained, in spite of the statements in the text-books.

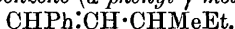
The cyanogen in the substance was estimated by treating it with water and magnesium powder, collecting the hydrogen cyanide which is evolved in aqueous potassium hydroxide, and titrating it with *N*/10 silver solution. Half of the liquid is eventually distilled over from the remaining magnesium, and then some dilute sulphuric acid is added through a stoppered funnel; the hydrogen evolved carries over the last traces of hydrogen cyanide. C. F. B.

Cyano-derivatives of Vanadium. EMIL PETERSEN (*Zeit. anorg. Chem.*, 1904, 38, 342—349).—Details of the preparation of potassium vanadiocyanide, $K_4V(CN)_6 \cdot 3H_2O$, previously described by the author (*Abstr.*, 1903, i, 612), are given. The *double salt* of potassium pyrovanadate and potassium cyanide, $K_4V_2O_7 \cdot 4KCN \cdot 14H_2O$, prepared by electrolysing a solution of potassium metavanadate and potassium cyanide and then allowing the salt to separate from the solution, which had been concentrated by evaporation, forms white, prismatic crystals, and gradually parts with hydrogen cyanide on exposure to the atmosphere. A. McK.

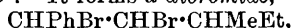
Synthesis of Hydrocarbons by Organo-magnesium Compounds and Methyl Sulphate. JOSEF HOUBEN (*Ber.*, 1904, 37, 488—489).—Controversial. A reply to Werner (*this vol.*, i, 25). A. McK.

Optically Active Benzene Hydrocarbons. AUGUST KLAGES and RICHARD SAUTTER (*Ber.*, 1904, 37, 649—655).—A large quantity of pure active amyl alcohol, prepared according to Marckwald's method (*Abstr.*, 1901, i, 248) ($[\alpha]_D - 5.89^\circ$ at 18°), was converted into pure amyl iodide, which has the following constants: sp. gr. 1.5232 at $15^\circ/4^\circ$, $[\alpha]_D + 5.78^\circ$ at 15° , boiling point 148° .

Active *methylpentenylbenzene* (α -phenyl- γ -methyl- Δ^a -pentene),

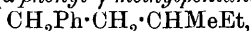


prepared by the interaction of benzaldehyde with a solution of amyl iodide and magnesium in ether, boils between 110° and 113° under 15 mm. pressure and has $[\alpha]_D + 43^\circ$ at 12° . When purified by conversion into the chloride and heating with pyridine, the phenylhexylene boils at 100 — 103° under 9.5 mm. pressure, has sp. gr. 0.8906 at $15^\circ/4^\circ$, and $[\alpha]_D + 50.3^\circ$ at 15° . It forms a *dibromide*,



which crystallises from alcohol in colourless needles, melts at 91 — 92° , and has $[\alpha]_D + 32.1^\circ$ at 15° in chloroform solution.

Active *hexylbenzene* (α -phenyl- γ -methylpentane),



prepared by reduction with sodium and alcohol, boils at 90 — 91° under 9 mm. and at 220° under 757 mm. pressure; it has a sp. gr. 0.8644 at $14.5^\circ/4^\circ$, $[\alpha]_D + 17.2^\circ$ at 14.5° , and forms a sulphonic acid, of which the barium salt crystallises in glistening plates. It is not racemised on heating with either sodium ethoxide or alcoholic potash. E. F. A.

Styrenes. IV. Styrenes Derived from Mesitylene. AUGUST KLAGES and CH. STAMM (*Ber.*, 1904, 37, 924—931. Compare *Abstr.*, 1902, i, 611, 666; 1903, i, 19).—Dimethylstyrenes of the type

$C_6H_2Me_3 \cdot CH \cdot CHR$ may be obtained from the acyl derivatives,
 $C_6H_2Me_3 \cdot CO \cdot CHR$,

by reduction to the carbinol, transformation into the corresponding chloride, and treatment with pyridine. These unsaturated hydrocarbons show no tendency to polymerise, and on treatment with sodium and ethyl alcohol are not reduced to the corresponding saturated hydrocarbons; the reduction may be accomplished by the aid of hydriodic acid and red phosphorus, except in the case of vinyl-mesitylene, which yields mesitylene and ethane.

The influence of the radicle R in mesityl ketones, $C_6H_2Me_3 \cdot COR$, is very pronounced in the decomposition of the ketones by boiling with syrupy phosphoric acid. Acetylmesitylene requires 1 hour, propionylmesitylene 4 hours, isobutyrylmesitylene and heptylmesitylene 8 hours.

The various substituents in the carbinols formed by the reduction of these ketones do not inhibit urethane formation. The following new compounds were prepared :

isoButyrylmesitylene boils at 142° under 20 mm. pressure and has a sp. gr. 0.9664 at $20^\circ/4^\circ$; *isovalerylmesitylene* boils at 151° under 20 mm. pressure and has a sp. gr. 0.9394 at $24^\circ/4^\circ$; *heptylmesitylene* boils at 172° under 15 mm. pressure and has a sp. gr. 0.9384 at $17^\circ/4^\circ$.

Mesitylethylcarbinol boils at 142° under 14 mm. pressure; *mesitylisopropylcarbinol* boils at $149\text{--}150^\circ$ under 19 mm. pressure and has a sp. gr. 0.9727 at $19^\circ/4^\circ$; *mesitylisobutylcarbinol* boils at 164° under 21 mm. pressure and has a sp. gr. 0.9440 at $24^\circ/4^\circ$; *mesitylhexylcarbinol* boils at 194° under 21 mm. pressure and has a sp. gr. 0.9462 at $17^\circ/4^\circ$.

Propenylmesitylene boils at $109\text{--}110^\circ$ under 18 mm. or at $223\text{--}224^\circ$ under 745 mm. pressure, has a sp. gr. 0.8988 at $21^\circ/4^\circ$, and n_D 1.5229 at 21° ; *isobutenylmesitylene* boils at $118\text{--}120^\circ$ under 14 mm. or at $226\text{--}227^\circ$ under 745 mm. pressure, has a sp. gr. 0.8900 at $18.8^\circ/4^\circ$, and n_D 1.5162 at 18.8° ; the *nitrosochloride* melts at 136° ; *pentenylmesitylene* boils at 136° under 22 mm. or at $239\text{--}240^\circ$ under 758 mm. pressure, has a sp. gr. 0.8901 at $20^\circ/4^\circ$, and n_D 1.5114 at 20° ; the *nitrosochloride* melts at 185° ; *heptenylmesitylene* boils at $170\text{--}171^\circ$ under 23 mm. or at $270\text{--}272^\circ$ under 760 mm. pressure, has a sp. gr. 0.8844 at $17^\circ/4^\circ$, and n_D 1.5136; the *nitrosochloride* melts at 160° . The *phenylurethane* of mesitylisopropylcarbinol melts at 169° . J. J. S.

Direct Reduction of Aromatic Halogen Derivatives by Nickel and Hydrogen. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1904, 138, 245—248).—Aromatic halogen derivatives can be directly reduced to the corresponding hydrocarbon by the action of hydrogen in the presence of reduced nickel under suitable conditions of temperature.

Chlorine Derivatives.—When a mixture of chlorobenzene vapour and excess of hydrogen is passed over reduced nickel at a temperature of 160° , a small quantity of cyclohexane is formed at first, but the nickel chloride, which is simultaneously produced, renders the nickel inert, and no further action takes place until the temperature is raised to 270° , when hydrogen chloride is evolved together with benzene and a small quantity of diphenyl; the probable course of the reaction being (1)

the formation of nickel chloride and its subsequent reduction, (2) the union of the phenyl residues with hydrogen to form benzene or with one another to form diphenyl; more than 40 per cent. of the final product is benzene. *m*-Dichlorobenzene, similarly treated, gives a mixture of 30 per cent. of benzene, 60 per cent. of chlorobenzene, and about 10 per cent. of the unchanged compound. *p*-Dichlorobenzene gives a reduction product consisting of 35 per cent. of benzene and 65 per cent. of chlorobenzene, whilst hexachlorobenzene gives a mixture containing trichlorobenzenes (chiefly 1:2:4-), dichlorobenzenes, and a small quantity of chlorobenzene and benzene.

Chlorinated aromatic derivatives containing an alkyl or hydroxyl radicle are more readily reduced (compare Liecke, *Abstr.*, 1900, i, 387), chlorotoluene giving a reduction product containing 50 per cent. of toluene, and 2:4:6-trichlorophenol a mixture of 75 per cent. of phenol with a little chlorophenols (chiefly ortho-), whilst the presence of an amino-group in the aromatic nucleus is even more effective, *o*- and *m*-chloroanilines being reduced at 200° to aniline hydrochloride and aniline. In the case of chloronitrobenzene, simultaneous reduction of the nitro-group (compare *Abstr.*, 1901, i, 195, 638; 1902, i, 701) and replacement of chlorine by hydrogen obtain, the reaction beginning at 180°, and the products being water, aniline hydrochloride, and aniline.

Bromine derivatives, although less readily reduced than the corresponding chloro-derivatives, yield similar products, thus, bromobenzene is reduced at 270° to benzene and diphenyl; 2:4:6-tribromophenol gives a mixture of phenol, *p*-bromophenol, and 2:4-dibromophenol.

Iodine Derivatives.—The reduction of iodobenzene by the action of hydrogen in contact with nickel can only be effected by passing alternately a mixture of iodobenzene and hydrogen, and hydrogen alone over the nickel at 270°, because the nickel iodide cannot be reduced by hydrogen in the presence of iodobenzene.

MARCELLIN BERTHELOT (*ibid.*, 248—249) refers to similar results which he obtained in 1868 by reducing aromatic compounds with hydrogen iodide, namely, (1) the production of benzene from chlorobenzene, hexachlorobenzene, or benzene hexachloride, (2) the hydrogenation of benzene, naphthalene, camphene, and terpene. M. A. W.

Crystallographic and Molecular Symmetry of Position Isomeric Benzene Derivatives. F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 406—408).—The six isomeric tribromotoluenes have been prepared in a form suitable for measurement; four of them are monoclinic, one rhombic, and one tetragonal, the last two being those with the bromine atoms in the vicinal position. Of the first four, there are two [$Br_3 = 2:3:5$ and $2:4:6$] which form mixed crystals in all proportions. The densities of the monoclinic forms do not greatly differ; the density of the rhombic isomeride is smaller, and that of the tetragonal isomeride still smaller.

The fifteen possible melting point lines of the binary mixtures of the six isomerides were determined. A. McK.

[Sulphur Derivatives of Diphenyl.] KALLE & Co. (D.R. P. 144464).—Tetranitrodiphenyl sulphide (Beilstein and Kurbatoff, Abstr., 1879, 230) is partially reduced on warming with sodium sulphide. When the product is fused with sodium sulphide and either dinitrophenylaminesalicic acid (Dierbach, Abstr., 1893, i, 211) or 2 : 4-dinitro-4'-hydroxydiphenylamine, greenish-black dyes are produced, dissolving readily in water. No such products are obtained when the original compounds are fused singly with sodium sulphide.

C. H. D.

Direct Hydrogenation of Aniline. Synthesis of *cyclo*Hexylamine and of Two New Amines. PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1904, 138, 457—460).—Aniline is directly hydrogenised in the presence of reduced nickel at 190°, the product consisting of *cyclo*hexylamine, *dicyclo*hexylamine, and *cyclo*hexylaniline in approximately equal proportions. (1) *cyclo*Hexylamine, $C_6H_{11}\cdot NH_2$, the normal product (compare Abstr., 1901, i, 195, 263; 1904, i, 156), is identical with the compound obtained by Baeyer by reducing *cyclo*hexanoxime (compare Abstr., 1894, i, 175), and by Markownikoff by reducing nitro*cyclo*hexane (compare Abstr., 1899, i, 23). It is a colourless liquid with an intense ammoniacal odour recalling that of conine, boils at 134° (corr.) under normal pressure, has a sp. gr. of 0.87 at 0°/0°, readily absorbs carbon dioxide from moist air to form a characteristic crystalline soluble carbonate; its hydrochloride crystallises in thin needles melting at 206°, very soluble in water or alcohol, slightly so in ether; it is a strong alkali turning litmus blue, and attacking the skin and corks. (2) *Dicyclo*hexylamine, $NH(C_6H_{11})_2$, formed from *cyclo*hexylamine according to the following equation, $2C_6H_{11}\cdot NH_2 = NH_3 + NH(C_6H_{11})_2$, is a colourless liquid with a similar, but much less pronounced, odour; it boils at 145° (corr.) under 30 mm. pressure, and at 250° under normal pressure, with slight decomposition and formation of *cyclo*hexylaniline, $NH(C_6H_{11})_2 = H_6 + NHPh\cdot C_6H_{11}$; it solidifies on cooling, forming prismatic crystals, melts at about 20°, has a sp. gr. 0.936 at 0°/0°, is slightly soluble in water, and very soluble in alcohol, ether, or benzene; it is alkaline towards litmus or phenolphthalein, precipitates silver oxide and copper hydroxide from their respective salts, absorbs carbon dioxide to form a crystalline carbonate, which is completely dissociated on drying in the air; the *hydrochloride* crystallises in beautiful, white needles, very soluble in water or alcohol, very slightly so in ether. (3) *cyclo*Hexylaniline, $NHPh\cdot C_6H_{11}$, formed by the partial destruction of the *dicyclo*hexylamine, is a yellow liquid with a faint odour, boils at 171° under 30 mm. and at 275° under normal pressure, with decomposition and formation of diphenylamine; it has a sp. gr. of 1.016 at 0°/0°, is very soluble in water, and solidifies on cooling, forming brilliant prisms or rhombic plates which melt at about 10°; the *hydrochloride* crystallises in tufts of slender needles, which are very soluble in water or alcohol, and become grey and then green when exposed to the air. *cyclo*Hexylaniline shows the chemical properties both of a fatty and

an aromatic amine, thus, it turns red litmus blue, but does not form a solid carbonate, and gives colour reactions with oxidising agents similar to those afforded by diphenylamine under the same conditions, namely, with concentrated hydrochloric acid and a drop of nitric acid, an intense blue colour changing through violet to green; with dilute sulphuric acid and a drop of chromic acid, a purple colour changing to chestnut-brown; with dilute sulphuric acid and a drop of nitric acid, a reddish-brown colour; with a concentrated solution of iodic acid, a magnificent purple colour changing to deep violet.

By the prolonged action of hydrogen on diphenylamine in the presence of reduced nickel at 190—210°, a liquid was obtained containing an appreciable quantity of *cyclohexylaniline* and *dicyclohexylamine*, together with benzene, aniline, and *cyclohexylamine*.

M. A. W.

Formation of Salts of Aromatic Bases with Dicarboxylic Acids. OTTO ANSELMINO (*Chem. Centr.*, 1904, i, 505—506; from *Ber. Deutsch. pharm. Ges.*, 13, 494—499).—In some of the following instances, the aromatic base combines with the dicarboxylic acid only in one proportion, namely, that of the acid salt. In these cases, variation of the proportions of acid and base does not affect the result either when the salt is prepared by direct combination of the acid and the base or by mixing aqueous, alcoholic, or ethereal solutions of the components; the same salt is also formed at 100° and at the ordinary temperature, and aqueous solutions of the acid are only able to combine with 1 mol. of the base.

Aniline and *p*-anisidine form normal or acid oxalates; the acid salt is converted into the normal salt by the action of boiling alcohol. *p*-Toluidine, methylaniline, *m*-toluidine, mesidine, and methyl-*o*-toluidine also form acid and normal salts, but the former are not affected by boiling with alcohol. Dimethylaniline, pyridine, and quinoline yield only acid oxalates, and with malonic acid, aniline and *p*-toluidine form only acid malonates. Aniline and *p*-anisidine yield acid succinates which are comparatively stable, whilst *p*-toluidine forms a rather unstable acid salt. Methylaniline, dimethylaniline, and pyridine do not combine with succinic acid, and attempts to prepare aniline and *p*-toluidine salts of sebacic acid also failed.

It appears, therefore, that the stronger acids form salts more readily than the weaker, whilst the weaker bases, on the other hand, combine more readily with acids than the stronger.

Aniline oxalate melts at 175°, aniline hydrogen oxalate at 163°, anisidine oxalate at 199°, anisidine hydrogen oxalate at 186°, *p*-toluidine oxalate at 183—184°, *p*-toluidine hydrogen oxalate at 178°, methyl-aniline oxalate at 113°, dimethylaniline hydrogen oxalate at 141°, pyridine hydrogen oxalate at 151—152°, and quinoline hydrogen oxalate at 105°. Aniline hydrogen malonate melts at 91—92° and *p*-toluidine hydrogen oxalate at 114°. Aniline hydrogen succinate melts at 122°, anisidine hydrogen succinate at 125°, and *p*-toluidine hydrogen succinate at 123—124°.

E. W. W.

Action of Organo-magnesium Compounds on Thiocarbimides and on Carbylamines. II. FRANZ SACHS and HERMANN LOEVY (*Ber.*, 1904, 37, 874—878. Compare *Abstr.*, 1903, i, 334).—*Thiophenylacetanilide*, $\text{NHPh}\cdot\text{CS}\cdot\text{CH}_2\text{Ph}$, obtained from magnesium benzyl bromide and phenylthiocarbimide, crystallises in pale yellow needles melting at 87° . *Thioacetyl-p-chloroanilide*, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{CSMe}$, melts at 143° ; *thioacetyl-p-phenetidine*, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CSMe}$, crystallises in yellow plates and melts at 99 — 100° ; *thiopropionyl-p-phenetidine* melts at 74 — 75° , and *thiobenzoyl-p-phenetidine* at 127° . All are readily soluble in most organic solvents, and also dissolve in dilute alkalis.

Dithiopropionylbenzidine and magnesium ethyl bromide yield the compound, $\text{C}_{12}\text{H}_8(\text{NH}\cdot\text{CSet})_2$, melting at 228 — 229° .

Thiobenzoylmethylamide, $\text{NHMe}\cdot\text{CSPH}$, obtained from magnesium phenyl bromide and methylthiocarbimide, crystallises in yellow, glistening needles and melts at 79° . *Thioacetylallylamide*, $\text{C}_3\text{H}_5\cdot\text{NH}\cdot\text{CSMe}$, is a yellow oil distilling at 135 — 136° under 17 mm. pressure. *Thiopropionylallylamide* is also an oil, and distils at 136° under 12 mm. pressure. Its dibromide crystallises in colourless needles and melts at 179° . *Thiobenzoylallylamide*, $\text{C}_3\text{H}_5\cdot\text{NH}\cdot\text{CSPH}$, distils at 214 — 215° under 17 mm. pressure and yields a dibromide melting at 208 — 209° .

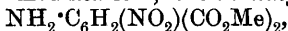
Benzaldehyde may be obtained by adding methylcarbylamine to an ice-cold ethereal solution of magnesium phenyl bromide, pouring into water and dilute sulphuric acid, and distilling the product with steam. The reaction is probably $\text{CH}_3\cdot\text{N}:\text{C} \rightarrow \text{CH}_3\cdot\text{N}:\text{CPh}\cdot\text{MgBr} \rightarrow \text{O}:\text{CHPh}$.
J. J. S.

Derivatives of *m*-Xylene. GIORGIO ERRERA and R. MALTESE (*Gazzetta*, 1903, 33, ii, 277—290).—On nitrating *m*-xylene with nitric acid of sp. gr. 1.48, 2:4-dinitro-1:3-xylene is produced as well as the 4:6-dinitro-compound, which is the principal product. 4:6-Dinitro-*m*-xylene is very resistant to oxidising agents, and when heated with nitric acid of sp. gr. 1.15 for 3 hours at 155 — 160° , only one-third is oxidised to form 4:6-dinitro-*m*-toluic acid, the remainder being unaffected; the acid obtained crystallises from benzene in transparent, yellow scales, melts at 171 — 171.5° , and gives an ethyl ester which crystallises from methyl alcohol in monoclinic prisms [$a:b:c = 1.61662:1:1$; $\beta = 61^\circ 0' 57''$] and melts at 61 — 62° .

4-Benzoylamino-6-nitro-*m*-xylene, prepared by benzoylating the corresponding base, crystallises from alcohol in white, silky needles melting at 200° . 4-Benzoylamino-2-nitro-*m*-xylene resembles it, but melts at 236° .

When 4-amino-6-nitro-*m*-xylene is boiled with acetic anhydride, a mixture of mono- and di-acetyl derivatives is obtained. The mono-acetyl derivative, $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Me}_2\cdot\text{NHAc}$, crystallises from alcohol in monoclinic plates [$a:b:c = 0.66953:1:1$; $\beta = 79^\circ 36' 20''$] and melts at 159° . The diacetyl derivative, $\text{NO}_2\cdot\text{C}_6\text{H}_2\text{Me}_2\cdot\text{NAc}_2$, crystallises from benzene in transparent, anorthic, elongated plates [$a:b:c = 1.04676:1:1.61337$; $\alpha = 93^\circ 3'$; $\beta = 80^\circ 5' 39''$; $\gamma = 64^\circ 56' 38''$] and melts at 115° . On oxidising either of these compounds with potassium permanganate, 4-acetylamino-6-nitroisophthalic acid is obtained, partial hydrolysis occurring in the case of the diacetyl derivative; the acid

crystallises from glacial acetic acid in opaque, white needles and melts and decomposes at 264° . 4-Amino-6-nitroisophthalic acid, prepared by hydrolysing the acetyl derivative, separates from boiling water in small, yellowish-brown crystals, or in nodules of light straw-coloured needles, melts and decomposes at 280° , and gives a lead salt existing in a red and a yellow modification; the dimethyl ester,



crystallises from methyl alcohol in hard, yellowish-brown, lustrous crystals and melts at 153° .

Methyl 4-amino-6-nitro-m-toluate [$\text{Me} : \text{CO}_2\text{Me} : \text{NH}_2 : \text{NO}_2 = 3 : 1 : 4 : 6$ or $3 : 1 : 6 : 4$] can be obtained by methylating the residue obtained after extracting 4-acetyl-amino-6-nitro-isophthalic acid from the product of oxidation of the foregoing acetylnitrotoluidines; it forms red crystals and melts at 128° . W. A. D.

Dibenzylideneacetone and Triphenylmethane. IV. ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1904, 37, 597—612. Compare Abstr., 1902, i, 380, 769; 1903, i, 811).—The following system of nomenclature is suggested for aminotriphenylmethane derivatives: $\text{OH} \cdot \text{CPh}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, carbinol; $\text{OH} \cdot \text{CPh}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \cdot \text{HCl}$, carbinol hydrochloride; $\text{CPh}_2\text{Cl} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, carbinol [carbiny] chloride, which is unstable, and is immediately transformed into $\text{CPh}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{HCl}$, the dye salt; $\text{CPh}_2\text{Cl} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \cdot \text{HCl}$, carbinol [carbiny] chloride hydrochloride.

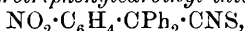
p-Aminotriphenylmethane is best purified by distillation under reduced pressure; it boils at 248° under 12 mm. pressure, and separates from benzene solution in large crystals containing benzene and melting at 83.5° . The acetyl derivative melts at 166 — 167° (Abstr., 1890, 1141; 1888, 56; 1891, 695), and on oxidation with chromic acid yields the acetyl derivative of the carbinol; when this is hydrolysed with hydrochloric acid, the amino-carbinol hydrochloride is obtained; it crystallises in pale orange-coloured, anhydrous plates; the free aminocarbinol has not been obtained in a crystalline form (compare Baeyer and Löhr, Abstr., 1890, 1141).

p-Aminotriphenylcarbiny] chloride hydrochloride, obtained when the carbinol hydrochloride is covered with dry ether and then saturated with dry hydrogen chloride, crystallises in colourless needles which are extremely hygroscopic. It dissolves in alcohol to a red solution, which slowly deposits colourless needles. When heated at 100° in a current of dry hydrogen, it yields the dye salt in the form of a deep orange-red powder which is soluble in chloroform. The picrate of the aminocarbinol, obtained by mixing benzene solutions of the components, crystallises in orange-coloured plates, and on treatment with pyridine yields the aminocarbinol.

The red picrate previously described is the picrate of the dye base, and on treatment with pyridine yields the polymeric anhydro-base, $(\text{C}_{19}\text{H}_{15}\text{N})_2$, which may also be obtained by decomposing the carbiny] chloride and the carbiny] chloride hydrochloride with pyridine. It crystallises from hot pyridine in long, flat, colourless needles, $(\text{C}_{19}\text{H}_{15}\text{N})_2 \cdot 3\text{C}_5\text{H}_5\text{N}$, which lose pyridine at 160° . With anhydrous acids, the base gives red salts, but with aqueous acids, colourless or yellow salts of the carbinol.

The *carbinyl thiocyanate* forms a *hydrochloride*,
 $\text{CNS} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \cdot \text{HCl}$,
 which crystallises in colourless needles.

The compound previously (*loc. cit.*) described as *p*-nitrotriphenylcarbinol is really impure *p*-nitrobenzophenone. *p*-Nitrobenzophenone chloride, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}_2\text{Cl}$, crystallises in yellow, rhombic plates, melts at $56-57^\circ$, and reacts with benzene and aluminium chloride yielding *p*-nitrotriphenylcarbinyl chloride, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}_2\text{Cl}$, which crystallises from light petroleum in colourless, glistening prisms melting at $92-93^\circ$. With alkalis, it yields *p*-nitrotriphenylcarbinol in the form of short prisms melting at $97-98^\circ$, and this, on reduction, gives the *p*-aminocarbinol. *p*-Nitrotriphenylcarbinyl thiocyanate,



crystallises from alcohol in colourless needles melting at $114-115^\circ$. *p*-Nitrotriphenylmethylphenylsulphone, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}_2 \cdot \text{SO}_2\text{Ph}$, crystallises from acetic acid in rhombic plates melting at $167-168^\circ$.

Diphenyl-p-anisylcarbinol anilide, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NPhPh}$, obtained by the action of diphenylanisylcarbinyl chloride (Abstr., 1903, i, 812) on aniline, crystallises in small plates melting at $138-139^\circ$; when heated for 20 hours with benzoic acid and a little benzene, it yields *ωω*-diphenylquinonemethane phenylimide, $\text{CPh}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NPh}$; this may be best purified by conversion into its *picrate*, $\text{C}_{31}\text{H}_{22}\text{O}_7\text{N}_4$, which crystallises in blackish-violet, flat needles, or the *sulphate*, which crystallises in black needles. The *hydrochloride*, $\text{C}_{25}\text{H}_{20}\text{NCl}$, crystallises in dark plates, and is soluble in hydrochloric acid saturated with ether. The free base crystallises in red prisms, melts at $133-138^\circ$, is unimolecular, and combines with sodium hydrogen sulphite to form a colourless sulphonate. It readily combines with water, yielding *p*-anilinotriphenylcarbinol, $\text{NPhPh} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$, as a colourless syrup which cannot be transformed back into the red quinoneimide. With methyl alcohol, the base yields *p*-anilinotriphenylcarbinyl methyl ether, $\text{NPhPh} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, which crystallises in colourless plates melting at 127° .

J. J. S.

Action of Sulphites on Aromatic Amino- and Hydroxy-compounds. HANS TH. BUCHERER (*J. pr. Chem.*, 1904, [ii], 69, 49-91. Compare Abstr., 1901, i, 695, 699; 1902, i, 91, 366, 718; 1903, i, 480).—As indicated previously, when treated with sodium hydrogen sulphite solution, amino- and hydroxy-derivatives of the naphthalene series both yield phenolic sulphites, from which alkalis produce phenols, whilst amines are formed with ammonium sulphite. Benzenoid amines and phenols do not give these reactions, with the exception of *m*-diamino- and *m*-dihydroxy-compounds; in these cases, however, the reaction is complicated by secondary reactions, probably of sulphonation.

With the diamionaphthalenes and sodium hydrogen sulphite, the main reaction consists in the conversion of one amino-group into a sulphiteresidue, thus, with naphthylene-1:8-diamine the 8-amino-*α*-naphthol sulphite produced is fairly stable, probably owing to the influence of the *peri*-position, and an analysis served to prove the unimolecular ratio of phenol to sulphurous radicle. The isomeric 5-amino-*α*-naphthol sul-

phite from naphthylene-1:5-diamine undergoes partial hydrolytic dissociation, so that 1:5-dihydroxynaphthalene is also produced. With dihydroxynaphthalenes, the formation of di-esters appears to be difficult, the mono-esters resulting from the reaction uniting slowly with diazo-compounds.

Although with sodium hydrogen sulphite 5-amino- α -naphthol gives the sulphurous ester of 1:5-dihydroxynaphthalene, 8-amino- α -naphthol gives chiefly 8-amino- α -naphthol sulphite. Of the isomeric 8-amino- α -naphthol-4- and -5-sulphonic acids, the 1:8:4-compound behaves similarly to 5-amino- α -naphthol, yielding the sulphurous ester of 1:8-dihydroxynaphthalene-4-sulphonic acid, and the 1:8:5-compound reacts similarly to 8-amino- α -naphthol, yielding the sulphurous ester of 8-amino- α -naphthol-5-sulphonic acid.

In the replacement of hydroxyl by the amino-group by means of ammonium sulphite and ammonia, with dihydroxy-compounds, the successive replacement of both hydroxy-groups is possible, excepting with certain *peri*-derivatives which display considerable stability towards sodium hydrogen sulphite, and in cases where the orientation of a substituting sulphonic acid radicle prevents reaction. As regards the latter phenomenon, the main conclusions are, that whilst the presence of a *para*-substituent facilitates, that of a *meta*-sulphonic group hinders the sulphite reactions. Thus these reactions occur more or less readily with 1:4-, 1:5-, 1:6-, 1:7-, 1:8-, 2:1-, 2:6-, 2:7-, and 2:8-aminonaphthalenesulphonic acids; with 1:4:6-, 1:4:7-, 1:4:8-, 1:5:7-, 1:6:8-, 2:1:6-, 2:3:6-, 2:3:7-, and 2:6:8-aminonaphthalenedisulphonic acids, and with 2:3:6:8-aminonaphthalenetrisulphonic acid; but reaction is difficult or absent with 1:2-, 1:3-, 1:2:4-, 1:2:5-, 1:3:7-, and 2:4:8-aminonaphthalene- and hydroxynaphthalenesulphonic acids.

G. D. L.

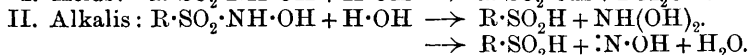
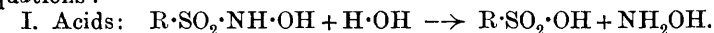
[*p*-Phenetidine- and *p*-Anisidine-*o*-sulphonic Acid.] AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 146655).—*p*-Phenetidine- and *p*-anisidine-*o*-sulphonic acids, prepared by heating the hydrogen sulphates of the bases or by boiling *p*-nitrophenetole or *p*-nitroanisole with sodium hydrogen sulphite, crystallise from water, and form crystalline, readily soluble sodium salts. They may be diazotised and combined with β -naphthol, and the azo-compounds thus obtained form red lakes with barium and aluminium hydroxides, &c.

C. H. D.

Hydroxamic Acids. ANGELO ANGELI, FRANCESCO ANGELICO, and FRANCESCO SCURTI (*Gazzetta*, 1903, **33**, ii, 296—311).—*Naphthalene-sulphohydroxamic acid*, $C_{10}H_7 \cdot SO_2 \cdot NH \cdot OH$, prepared in the same way as benzenesulphohydroxamic acid (Piloty, *Abstr.*, 1896, i, 555), crystallises from water in colourless plates, melts and decomposes at 153° , and is converted by aqueous potassium hydroxide into naphthalene-2-sulphinic acid and nitroxyl, $:N \cdot OH$, which can be fixed by means of benzaldehyde or piperonaldehyde, benzhydroxamic and piperonylhydroxamic acids being respectively formed; the production of naphthalene-2-sulphinic acid instead of naphthalene-1-sulphinic acid is particularly noteworthy. When naphthalene-1-sulphohydroxamic acid is

hydrolysed by alcoholic sodium ethoxide in presence of nitrosobenzene, the nitroxyl combines with the latter to form nitrosophenylhydroxylamine.

The hydrolysis of naphthalene-1-sulphohydroxamic acid by acids is different to that effected by alkalis, naphthalene-1-sulphonic acid being formed together with a hydroxylamine salt; the latter can be identified by its giving an oxime with piperonaldehyde. The two kinds of hydrolysis are due to the hydrogen ions being operative in the case of acids, and hydroxyl ions in that of alkalis, as shown by the equations:



When naphthalene-1-sulphohydroxamic acid is boiled with acetic anhydride, it gives a *diacetyl* derivative, $\text{C}_{10}\text{H}_7\cdot\text{SO}_2\cdot\text{NOAc}_2$, which melts at 104° and, like the parent substance, is resolved by alkalis into naphthalene-2-sulphinic acid and nitroxyl.

Benzene-m-disulphohydroxamic acid, $\text{C}_6\text{H}_4(\text{SO}_2\cdot\text{NH}\cdot\text{OH})_2$, prepared from benzene-*m*-disulphonic chloride, crystallises from benzene with $\frac{1}{2}$ mol. of the solvent and melts at 152° ; like the foregoing compound, it liberates nitroxyl in alkaline solution.

Dinaphthalene-1-sulpho-hydroxamic acid, $\text{OH}\cdot\text{N}(\text{SO}_2\cdot\text{C}_{10}\text{H}_7)_2$, prepared by acidifying a solution containing sodium nitrite and sodium naphthalene-1-sulphinic acid, crystallises from methyl alcohol, melts at 102° , and is transformed by cold alkalis into the isomeric *dinaphthalene-2-sulpho-hydroxamic acid*, which melts at 115° and is also obtained by the direct interaction of nitrous acid and naphthalene-2-sulphinic acid; the final action of alkalis on both acids is to regenerate the parent sulphinic acid.

Dibenzenesulphohydroxamic acid, $\text{OH}\cdot\text{N}(\text{SO}_2\text{Ph})_2$, is converted similarly by cold aqueous sodium hydroxide into nitrous and benzenesulphinic acids, but by warm 80 per cent. sulphuric acid it is resolved into benzenesulphonic acid and hydroxylamine. The different action of alkalis and of acids is explained in the same way as in the case of the simple sulphohydroxamic acids.

Trinaphthalenesulphohydroxamic acid, $\text{NO}(\text{SO}_2\cdot\text{C}_{10}\text{H}_7)_3$, prepared by the action of warm nitric acid of sp. gr. 1.18 on dinaphthalene-1-sulphohydroxamic acid, is a crystalline powder which is almost insoluble in all solvents and darkens at about 270 – 280° , subsequently melting to a black liquid. It is resolved by alkalis seemingly into nitric acid and naphthalenesulphinic acid, although the latter cannot be isolated owing to its undergoing decomposition. With acids, on the other hand, it affords hydroxylamine.

W. A. D.

[Chloronitroaminophenols.] CHEMISCHE FABRIK VORM. SANDOZ (D.R.-P. 147060).—6-*Chloro-2-nitro-4-aminophenol*, prepared by the nitration of 6-chloro-4-aminophenol in sulphuric acid solution, melts at 130° . Intensely black dyes are obtained by diazotising it, combining with α -naphthylamine-6- or -7-sulphonic acid, again diazotising, and combining with α -naphthol-4- or -5-sulphonic acid. 4-*Chloro-6-nitro-2-aminophenol*, prepared by the partial reduction of the corresponding

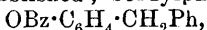
chlorodinitrophenol and melting at 152° , and the already known 6-chloro-4-nitro-2-aminophenol do not produce this result.

C. H. D.

Separation of *m*- and *p*-Cresols. CHEMISCHE FABRIK LADENBURG (D.R.P. 148703).—The separation of *m*- and *p*-cresols by partial sulphonation with sulphuric acid is imperfect, and involves the use of large quantities of sulphuric acid. It is found that pure *m*-cresol is rapidly sulphonated on heating with 4 parts of sodium hydrogen sulphate at 100° , the whole solidifying to a mass of crystalline leaflets. *p*-Cresol, on the other hand, is only sulphonated by this method at 160 – 180° . Crude cresol is therefore heated with sodium hydrogen sulphate at 100 – 110° , and dissolved in water, when unaltered *p*-cresol separates as an oily layer, and sodium *m*-cresol-sulphonate crystallises from the solution. Should the free *m*-cresol be required, superheated steam at 180° is passed into the solution, a temperature of 130 – 140° being sufficient when free sulphuric acid is employed.

C. H. D.

Condensations in presence of Metals and Metallic Chlorides [Benzylphenol]. MARUSSIA BAKUNIN (*Gazzetta*, 1903, 33, ii, 454–460. Compare Abstr., 1903, i, 818).—The condensation between phenol and benzyl chloride, effected by granulated zinc, in various solvents is described, and the best conditions for preparing benzylphenol, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Ph}$, are established; benzylphenyl benzoate,

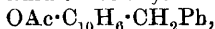


melting at 86 – 87° , was prepared by heating benzylphenol with benzoic acid and phosphoric oxide in benzene solution. A similar compound, melting at 155 – 156° , was obtained from β -nitrophenyl-cinnamic acid, but was not analysed.

In alcoholic solution, zinc condenses benzyl chloride with *p*-aminophenol, giving the *dibenzyl* derivative, $\text{OPh}\cdot\text{N}(\text{CH}_2\text{Ph})_2$, which is insoluble in alkali and crystallises from benzene in needles melting at 125 – 126° ; its structure has not yet been determined. W. A. D.

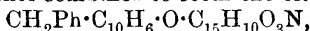
Action of Benzyl Chloride on Naphthols. Formation of Anthracene as a By-product. MICHELE BARBERIO (*Gazzetta*, 1903, 33, ii, 460–466).—Fruitless attempts are described to prepare benzyl- α -naphthol and benzyl- β -naphthol by the direct interaction of benzyl chloride and the naphthol in presence of zinc chloride (compare following abstracts); in the case of α -naphthol, a small quantity of anthracene is formed. W. A. D.

Benzyl- α -naphthol and Derivatives. MARUSSIA BAKUNIN and MICHELE BARBERIO (*Gazzetta*, 1903, 33, ii, 467–478).—*Benzyl- α -naphthol*, $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}_2\text{Ph}$, prepared by condensing α -naphthol with benzyl chloride in warm benzene solution by means of zinc, crystallises from benzene in white, acicular prisms and melts at 125 – 126° ; the yield is only 30 per cent. that of theory, oily substances, insoluble in alkali, being produced simultaneously. The *acetyl* derivative,



crystallises from benzene in small, snow-white needles and melts at 87—88°; the corresponding *benzoyl* derivative crystallises from alcohol in white needles melting at 102—103°.

With phenyl-*p*-nitrocinnamic acid in presence of phosphoric oxide, benzyl- α -naphthol combines to form the *ester*,



which crystallises from acetone in long, silky, straw-coloured needles melting at 155—156°; the analogous *compound*, $\text{C}_{10}\text{H}_7\cdot\text{O}\cdot\text{C}_{15}\text{H}_{10}\text{O}_3\text{N}$, of α -naphthol separates from alcohol in flat needles and melts at 126—127°. The compound obtained from benzyl- α -naphthol and salicylic acid forms long, yellow needles and melts at 85—86°.

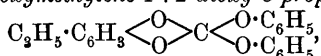
With nitric acid in glacial acetic acid solution, benzyl- α -naphthol gives a *mononitro*-derivative, which decomposes at 80—90° and has not yet been obtained crystalline. W. A. D.

Benzyl- β -naphthol and Derivatives. MARUSSIA BAKUNIN and GAETANO ALTIERI (*Gazzetta*, 1903, 33, ii, 487—492. Compare preceding abstracts).—*Benzyl- β -naphthol*, $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}_2\text{Ph}$, obtained, with a yield of 25 per cent., by condensing benzyl chloride with β -naphthol by means of zinc in benzene or alcoholic solution, crystallises from glacial acetic acid in long, white needles, and melts at 115—116°; the *acetyl* derivative crystallises from alcohol in well-formed prisms melting at 40°, and the *benzoyl* derivative forms white, silky needles and melts at 95—97°. The *ester*, $\text{CH}_2\text{Ph}\cdot\text{C}_{10}\text{H}_6\cdot\text{O}\cdot\text{C}_{15}\text{H}_{10}\text{O}_3\text{N}$, prepared by means of phenyl-*p*-nitrocinnamic acid and phosphoric oxide, crystallises from alcohol in needles and melts at 145°. W. A. D.

Preparation of Hydroxydiaryl Sulphides. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 147634).—Hydroxydiaryl sulphides are prepared by heating arylsulphinic acids with phenols or phenol derivatives at 100—150°. Benzenesulphinic acid and phenol form *hydroxyphenyl sulphide*, $\text{C}_6\text{H}_5\cdot\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, a brown oil with faint, aromatic odour, soluble in water. It is separated from impurities by means of methyl iodide and sodium ethoxide, forming the *methyl ether*, a colourless oil with leek-like odour, boiling at 180—185° under 12 mm. pressure. *Hydroxyphenylsulphide-o-carboxylic acid*, prepared from benzenesulphinic acid and salicylic acid, crystallises from dilute acetic acid in small needles and melts at 168°, dissolving sparingly in water and giving a violet coloration with ferric chloride. *Hydroxyphenyl p-tolyl sulphide*, obtained from *p*-toluenesulphinic acid and phenol, is a yellow oil, sparingly soluble in water; *hydroxyphenyl-p-tolyl-sulphide-o-carboxylic acid* crystallises from dilute acetic acid in slightly yellow needles and melts at 162—164°. Similar products are obtained from the cresols. C. H. D.

Dichloromethylene-1 : 2-dioxy-5-propylbenzene and 5-Propylcatechol Carbonate. RAYMOND DELANGE (*Compt. rend.*, 1904, 138, 423—425. Compare Abstr., 1900, i, 289).—When dihydro-afrole (1 mol.) is heated with phosphorous pentachloride (2 mols.) until the evolution of hydrogen chloride ceases and the product submitted to fractional distillation, *dichloromethylene-1 : 2-dioxy-5-propylbenzene*,

$\text{C}_3\text{H}_7 \cdot \text{C}_6\text{H}_5 \begin{smallmatrix} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{smallmatrix} \text{CCl}_2$, was isolated as a colourless oil, which fumes in the air and boils at $142\text{--}145^\circ$ under 10 mm. pressure. When boiled with water, the carbonate of propylcatechol is formed as a primary product which is immediately decomposed by the hydrochloric acid present, giving 5-propylcatechol. When the dichloride is allowed to drop slowly into absolute ethyl alcohol, ethyl chloride is evolved and 5-propylcatechol carbonate formed; at the boiling point of alcohol, this carbonate is decomposed giving the free catechol and ethyl carbonate. With phenol, *diphenoxyethylene-1 : 2-dioxy-5-propylbenzene*,

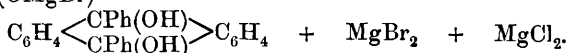
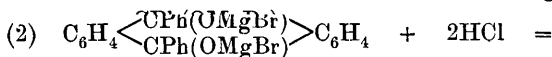
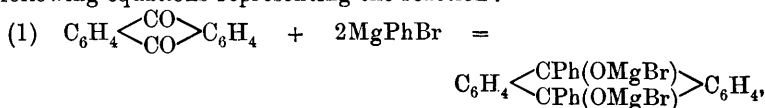


is produced; it is a liquid which boils at $256\text{--}258^\circ$ under 17 mm. pressure. With acetic anhydride, the dichloride yields acetyl chloride and the catechol carbonate; acetic acid gave the same products. The carbonate of 5-propylcatechol, which is formed in the foregoing reactions, is a liquid boiling at $139\text{--}141^\circ$ under 13 mm. pressure. It reacts with primary and secondary amines giving urethanes of the type $\text{OH} \cdot \text{C}_6\text{H}_3\text{Pr} \cdot \text{O} \cdot \text{CO} \cdot \text{NR}_1\text{R}$. That derived from aniline melts at 142° , that from *p*-phenetidine at 122° , and that from methylaniline at 110° .

S. S.

Action of Magnesium Phenyl Bromide on Anthraquinone. 9 : 10-Dihydroxy-9 : 10-diphenyldihydroanthracene.

ALBIN HALLER and ALFRED GUYOT (*Compt. rend.*, 1904, 138, 327—329. Compare Abstr., 1903, i, 200, 348; this vol., i, 83, 346).—By means of Grignard's synthetical method, 9 : 10-dihydroxy-9 : 10-diphenyldihydroanthracene (9 : 10-diphenyldihydroanthran-9 : 10-diol) can be obtained from magnesium phenyl bromide and anthraquinone, the following equations representing the reaction :



Owing to the sparing solubility of anthraquinone in ether, the yield is only 10 per cent. of the theoretical, and the new compound is separated from the unchanged anthraquinone by extraction with boiling methyl alcohol, from which it crystallises in long, colourless, brilliant needles containing alcohol of crystallisation; the crystals are, however, so efflorescent that the amount of alcohol has not been estimated.

The substance, when freed from alcohol, is a white powder melting at 242° (uncorr.); it is very sparingly soluble in most organic solvents, dissolves in concentrated sulphuric acid forming an intense indigo-blue coloration, persistent for several days in the cold, but rapidly becoming orange-yellow when warmed; in glacial acetic acid solution, it exhibits a violet fluorescence, and on the addition of a drop of hydrochloric acid a highly characteristic precipitate in the form of spangles, is produced,

which melts at a much lower temperature than the original compound, and seems to contain chlorine. M. A. W.

Reduction of Triphenylcarbinol and its Homologues to the Corresponding Triphenylmethanes. SALOMON F. ACREE (*Ber.*, 1904, 37, 616—617).—Only hexaphenylethane is obtained when trimethylcarbinol is reduced with stannous chloride (Ullmann and Borsum, *Abstr.*, 1902, i, 755; Gomberg, 1903, i, 244). Triphenylmethane, however, is readily obtained by the reduction of triphenylcarbinol or triphenylbromomethane in boiling alcoholic solution with tin and hydrochloric acid, the latter being gradually added. In the same way, diphenyl-*a*-naphthylmethane (Lehne, *Abstr.*, 1880, 478) is obtained from diphenyl-*a*-naphthylcarbinol. C. H. D.

Elimination of Carbon Dioxide from Tertiary Acids by means of Concentrated Sulphuric Acid. (Préparation of Diphenyl-*p*-tolylcarbinol.) AUGUSTIN BISTRZYCKI and JOSEPH GYR (*Ber.*, 1904, 37, 655—664. Compare *Abstr.*, 1901, i, 701 and 716).—Diphenyl-*p*-tolylcarbinol, $C_6H_4Me \cdot CPh_2 \cdot OH$, formed quantitatively by the action of cold sulphuric acid on diphenyltolylacetic acid, crystallises from benzene in colourless octahedra, melts at 72—73°, and boils at 227° under 12 mm. pressure. Oxidation with chromic acid mixture converts it into triphenylcarbinol-*p*-carboxylic acid, whilst on reduction diphenyl-*p*-tolylmethane is formed.

p-Hydroxytriphenyl-*p*-tolylmethane, prepared by condensing diphenyltolylcarbinol with phenol, crystallises in colourless needles melting at 201°, and dissolves in normal potassium hydroxide on boiling; it forms an *acetox*y-derivative which crystallises from alcohol in colourless needles and melts at 135°. *p*-Acetoxytetraphenylmethane, $CPh_3 \cdot C_6H_4 \cdot OAc$, crystallises in bunches of needles melting at 175°. Diphenyl-*p*-tolylchloromethane forms colourless, rhombic plates melting at 99°.

Diphenyl-*p*-tolylcarbinol can also be prepared by Grignard's methods, by the interaction of magnesium phenyl bromide and methyl *p*-toluate in ethereal solution.

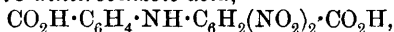
p-Carboxytriphenylacetic acid, $CO_2H \cdot C_6H_4 \cdot CPh_2 \cdot CO_2H$, prepared by the oxidation of diphenyltolylacetic acid with permanganate, crystallises in transparent prisms melting at 246—247° and forms a *disilver* salt. When heated with sulphuric acid, the known triphenylmethane-*p*-carboxylic acid is formed. E. F. A.

Derivatives of 2-Chloro-3:5-dinitrobenzoic Acid. III. ATTILIO PURGOTTI and C. LUNINI (*Gazzetta*, 1903, 33, ii, 324—335. Compare Purgotti and Contardi, *Abstr.*, 1902, i, 777, 778).—2-*o*-Toluidino-3:5-dinitrobenzoic acid, $C_6H_4Me \cdot NH \cdot C_6H_2(NO_2)_2 \cdot CO_2H$, prepared by boiling 2-chloro-3:5-dinitrobenzoic acid with alcoholic *o*-toluidine, crystallises from boiling alcohol in orange-yellow needles, melts at 171—172°, and gives a red, crystalline *potassium* salt with $1H_2O$. The analogous *m*-toluidino- and *p*-toluidino-derivatives are similar and melt at 203° and 220° respectively; the *potassium* salt of the latter crystallises with $2H_2O$.

2- α -Naphthylamino-3:5-dinitrobenzoic acid separates from alcohol as a dull red, crystalline powder and melts and decomposes at 226°; the analogous β -naphthylamine derivative melts and decomposes at 210°.

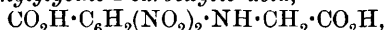
2-Ethylanilino-3:5-dinitrobenzoic acid, $\text{NEtPh}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{CO}_2\text{H}$, separates from alcohol in minute, yellow crystals melting at 150—151°.

2-Anthranilo-3:5-dinitrobenzoic acid,



prepared by means of anthranilic acid, separates from glacial acetic acid in small, orange-yellow crystals and melts at 251—252°; the corresponding compounds from *m*- and *p*-aminobenzoic acids crystallise from acetic acid and melt respectively at 273° and 264—265°.

3:5-Dinitrophenylglycine-1-carboxylic acid,



prepared from 2-chloro-3:5-dinitrobenzoic acid and glycine, crystallises from acetic acid in yellow needles and melts at 186—187°; it forms acid and normal salts; the *disilver* salt is a reddish-yellow powder which is stable in the light.

3:5-Dinitro-2-sulphobenzoic acid, $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{CO}_2\text{H}$, prepared by the action of sodium sulphite on 2-chloro-3:5-dinitrobenzoic acid, separates from water in minute crystals. W. A. D.

Nitrosobenzoic Acids. FREDERICK J. ALWAY (*Ber.*, 1904, 37, 333—335).—*p*-Nitrosobenzoic acid, $\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, is prepared by reducing *p*-nitrobenzoic acid in alcoholic solution by zinc dust and acetic acid, and adding ferric chloride to the solution of *p*-hydroxylaminobenzoic acid so obtained at a temperature of 45°; it forms a yellow powder, which is very sparingly soluble in the usual solvents and darkens above 250° without melting; with aniline, it combines to form azobenzene-*p*-carboxylic acid.

m-Nitrosobenzoic acid, obtained similarly from *m*-nitrobenzoic acid, is a white powder, which darkens above 230°, does not melt, and combines with *p*-toluidine to form toluene-*p*-azo-*m*-benzoic acid. W. A. D.

Stability of Anthranilic Acid and some of its Derivatives. BRONISLAW PAWLEWSKI (*Ber.*, 1904, 37, 592—596).—The following numbers give the percentage of anthranilic acid decomposed when heated for an hour at the given temperature:

| | | | | | | |
|-----------|------|------|------|------|------|------|
| Temp. | 150° | 160° | 170° | 180° | 190° | 200° |
| Per cent. | 23.9 | 47.7 | 72.6 | 76.8 | 88.3 | 96.2 |

The decomposition is complete after 1 hour at 205—210°.

Benzylaminobenzoic acid (Abstr., 1883, 1009) may be obtained by boiling a toluene solution of anthranilic acid with the requisite amount of benzyl chloride.

o-Nitrobenzylaminobenzoic acid, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, obtained by boiling an alcoholic solution of the constituents, crystallises in golden-yellow needles, melts at 205—206°, and is readily soluble in most organic solvents with the exception of benzene and light petroleum. The corresponding *p*-nitro-derivative melts at 208—210°.

o-Benzylideneaminobenzoic acid, obtained from the acid and *o*-nitrobenzaldehyde, crystallises in brick-coloured needles, melts at 167—168°, and dissolves readily in most solvents with the exception of ether and light petroleum. The isomeric *m*-nitro-compound melts at 198—200°. *Cinnamylideneaminobenzoic acid*, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, crystallises in golden-yellow plates melting at 163—164°. *Salicylideneaminobenzoic acid*, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, obtained from anthranilic acid and salicylaldehyde, melts at 202—204°, and *vanillideneaminobenzoic acid*, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, forms a canary-yellow, amorphous mass melting at 172—174° J. J. S.

Preparation of Diphenylaminedicarboxylic Acids. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 148179).—The production of diphenylamine-2:2'-dicarboxylic acid from alkali *o*-chlorobenzoates and ammonia in presence of copper salts (this vol., i, 168) is not a primary reaction, but is due to the action of the anthranilic acid first formed on the unaltered *o*-chlorobenzoate. Other aminobenzoic acids also react with *o*-chlorobenzoic acid when the alkali salts are heated with copper or copper salts at 115—120°. *m*-Aminobenzoic acid forms *diphenylamine-2:3'-dicarboxylic acid*, melting and decomposing at 281—282°, after previous sintering, and *p*-aminobenzoic acid forms *diphenylamine-2:4'-dicarboxylic acid*, melting and decomposing at 282—283°, and dissolving more readily in alcohol than its isomerides. C. H. D.

Preparation of Phenylglycine-*o*-carboxylic Acid from Sulphophenylglycine-*o*-carboxylic Acid. KALLE & Co. (D.R.-P. 147228).—The sulpho-group may be eliminated from sulphophenylglycine-*o*-carboxylic acid by electrolysis in alkaline or neutral solution in the manner described for sulphoanthranilic acid (this vol., i, 159), a diaphragm being employed. Very little hydrolysis occurs in slightly acid solutions. C. H. D.

Preparation of Acetylphenylglycine-*o*-carboxylic Acid. DANIEL VORLÄNDER & ERICH MUMME (D.R.-P. 147633).—Phenylglycine-*o*-carboxylic acid is not readily acetylated by the ordinary methods, coloured condensation products being formed. The reaction takes place very readily, however, in presence of sulphuric acid or hydrogen chloride, especially when acetic anhydride is employed (compare Vorländer and Weissbrenner, Abstr., 1900, i, 295). C. H. D.

Preparation of Ethyl 2:6:6-Trimethylcyclo- Δ^2 -hexene-4-one-1-carboxylate. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 148080).—The sodium compound of ethyl acetoacetate condenses with ethyl isopropylideneacetoacetate in cold alcoholic solution, forming sodium ethyl carbonate and *ethyl 2:6:6-trimethylcyclo- Δ^2 -hexene-4-one-1-carboxylate*, $\text{CH}_2\cdot\text{CMe}_2\cdot\text{CH}\cdot\text{CO}_2\text{Et}$
 $\text{CO}\cdot\text{CH}=\text{CMe}$, a colourless or yellow oil, with faint aromatic odour, boiling at 146—148° under 16 mm. pressure. C. H. D.

Alkyloxyalkyl Esters of Salicylic Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 146849. Compare Abstr., 1903, i, 485).—Halogen-dialkyl ethers, having the formula $X \cdot CHR' \cdot OR$ (where X =halogen, R and R' =the same or different alkyls), react with metallic salicylates, forming alkyloxyalkyl salicylates. Thus α -chloroethyl methyl ether and sodium salicylate form *methoxyethyl salicylate*, $OH \cdot C_6H_4 \cdot CO_2 \cdot CHMe \cdot OMe$, an almost colourless oil with faintly aromatic odour. On heating above 100° , acetaldehyde is evolved. Water, acids, or alkalis hydrolyse it to methyl alcohol, acetaldehyde, and salicylic acid. In similar manner, α -chlorodiethyl ether forms *ethoxyethyl salicylate*, $OH \cdot C_6H_4 \cdot CO_2 \cdot CHMe \cdot OEt$, a yellow oil, resembling the methoxy-ester. C. H. D.

Reduction of Indigotin and its Bromo-derivatives. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 139567 and 145602).—Indigotin may be reduced to indigo-white by electrolysis at about 70° in presence of sulphites, employing a current density of 4 amperes per sq. dm. The reaction depends on the intermediate formation of hyposulphites. Bromo- and dibromo-derivatives of indigotin may be reduced in similar manner, no portion of the bromine being removed. The leuco-compounds are obtained in the solid and stable form. C. H. D.

***o*-Phenoxybenzoic Acids.** ROBERT FOSSE and A. ROBYN (*Bull. Soc. chim.*, 1904, [iii], 31, 264—267).—5 : 4'-*Dimethyl-o-phenoxybenzoic acid*, $C_6H_4Me \cdot O \cdot C_6H_4Me \cdot CO_2H$, prepared by heating *p*-tolyl carbonate with a small quantity of sodium carbonate at 200° , and hydrolysing with sodium hydroxide dissolved in alcohol, the *p*-tolyl ester first produced, is crystalline, and melts at 113 — 114° . When heated with sulphuric acid, it is converted into 2 : 7-*dimethyldiphenopyrone* [2 : 7-*dimethylxanthone*], $C_6H_3Me \cdot \begin{smallmatrix} CO \\ \diagup \quad \diagdown \\ O \end{smallmatrix} \cdot C_6H_3Me$, which crystallises from alcohol in light yellow needles and melts at 142° .

3 : 2'-*Dimethyl-o-phenoxybenzoic acid*, similarly prepared from *o*-tolyl carbonate, melts at 115° , and, when heated with sulphuric acid at 100° , is converted into 4 : 5-*dimethyldiphenopyrone*, which melts at 172° .

T. A. H.

Condensation of Benzilic Acid with Phenols. R. GEIPERT (*Ber.*, 1904, 37, 664—673).—The lactone of 2-hydroxy-4 : 5-*dimethyltriphenylacetic acid*, $CPh_2 \cdot \begin{smallmatrix} C_6H_2Me_2 \\ \diagup \quad \diagdown \\ CO \end{smallmatrix} \cdot O$, produced by the combination of benzilic acid and *o*-xylenol in presence of tin tetrachloride, crystallises from acetic acid in plates, melts at 178° , and is insoluble in cold dilute sodium carbonate; it forms a *monobromo-derivative* crystallising in colourless needles melting at 161° .

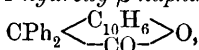
The lactone of 2-hydroxy-3 : 5-*dimethyltriphenylacetic acid*, which crystallises in colourless plates melting at 170° , is obtained from *m*-xylenol; *p*-xylenol, on the other hand, yields 4-hydroxy-2 : 5-*dimethyltriphenylacetic acid*, $OH \cdot C_6H_2Me_2 \cdot CPh_2 \cdot CO_2H$, which crystallises in plates,

decomposes at 236—237°, and is soluble in dilute sodium carbonate; the *acetoxy*-derivative melts and decomposes at 230—231°, and forms a sodium salt, whilst the *monobromo*-derivative forms yellow plates melting at 232—235°.

4-*Hydroxy-2-methyl-5-isopropyltriphenylacetic acid*, formed on combining benzoic acid and thymol, crystallises in prisms and melts at 197—198°. *Methyl 4-methoxy-2-methyl-5-isopropyltriphenylacetate* forms large, transparent prisms melting at 145—146°.

4-*Hydroxy-5-methyl-2-isopropyltriphenylacetic acid*, derived from carvacrol, crystallises in prisms and melts and decomposes at 241°; it is a much weaker acid than its isomeride derived from thymol, and forms an easily soluble sodium salt. *Methyl 4-methoxy-5-methyl-2-isopropyltriphenylacetate* forms short prisms melting at 137—138°.

The *lactone* of *diphenyl-1-hydroxy-β-naphthylacetic acid*,



produced by condensation with α -naphthol, crystallises in colourless prisms, softens at 145°, and melts and decomposes at 190°; it forms a *monobromo*-derivative, crystallising in large, transparent crystals melting at 205°, and a *mononitro*-derivative melting at 241°. With β -naphthol, benzoic acid forms the *lactone* of *diphenyl-2-hydroxy-α-(1)-naphthylacetic acid*, $\text{CPh}_2 \left\langle \begin{array}{c} \text{C}_{10}\text{H}_6 \\ \text{CO} \end{array} \right\rangle \text{O}$, which is sparingly soluble in alcohol, melts at 183°, and forms a *monobromo*-derivative, crystallising from acetic acid in long prisms melting at 162—164°. E. F. A.

Action of Nitric Acid on β -Resorcylic Acid and its Derivatives. FRANZ VON HEMMELMAYR (*Monatsh.*, 1904, 25, 21—45).—By the action of nitric acid on β -resorcylic acid, the author has obtained styphnic acid and tribasic nitro- β -resorcylic acid, which is very difficult to methylate, but easier to acetylate, although in the latter case only one of the hydroxyl groups is substituted.

Nitro-β-resorcylic acid, $\text{C}_7\text{H}_5\text{O}_6\text{N}$, crystallises from water in straw-yellow leaflets or almost colourless needles, containing water of crystallisation and melting at 215°. The following derivatives were prepared: the *disodium*, *trisodium*, *ammonium*, *diammonium*, *barium* (+ 3 H_2O), *dibarium* (+ 10 H_2O), *silver*, and the *disilver* salts; the *methyl ester*, which crystallises from methyl alcohol in shining leaflets, melting at 167°, and dissolves in ammonia solution, giving an orange-yellow liquid, which, with barium chloride, gives slender, yellow needles of the *compound*, $\text{C}_8\text{H}_5\text{O}_6\text{NBa}$. The *acetyl derivative*, $\text{C}_9\text{H}_7\text{O}_7\text{N}$, was obtained in impure crystals melting at 150°.

Reduction of nitro- β -resorcylic acid by means of tin and hydrochloric acid yields *amino-β-resorcylic acid hydrochloride*, $\text{C}_7\text{H}_7\text{O}_4\text{N}\cdot\text{HCl}$, which separates in bluish-green crystals (with 2 H_2O), melting and decomposing at 212—213°; when boiled with water, this hydrochloride yields the free *amino-acid*, which crystallises from water in microscopic prisms (+ H_2O), melting at 193°, and is soluble in acetic acid, nitric acid, or alkali solution; the *sulphate*, $(\text{C}_7\text{H}_7\text{O}_4\text{N})_2\cdot\text{H}_2\text{SO}_4$, separates in bunches of acicular crystals, melting and decomposing at 226°.

When heated to above 190°, amino- β -resorcylic acid yields a very

dark blue mass, exhibiting a copper-red lustre; the alcoholic solution of this substance dyes silk blue, and when mixed with water assumes a red fluorescence, and deposits dark blue flocks; with hot water, it gives a purple solution, and with alkalis a dark blue liquid, which becomes red on adding hydrochloric acid.

Diazotisation of amino- β -resorcylic acid yields a red, crystalline powder, probably diazo- β -resorcylic acid. T. H. P.

Bismuthoprotocatechuic Acid. PAUL THIBAUT (*Bull. Soc. chim.*, 1904, [iii], 31, 176—178. Compare Abstr., 1902, i, 101; 1903, i, 633, 701, 761, and this vol., i, 166).—The author has prepared the bismuthoprotocatechuic acid, $\text{OH} \cdot \text{Bi} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C}_6\text{H}_3 \cdot \text{CO}_2\text{H}$, described by Richard (Abstr., 1900, i, 593), by the addition of bismuth lactate, basic nitrate, or oxide to hot aqueous solutions of protocatechuic acid. It crystallises in microscopic, citron-yellow, stellate groups of pyramids, and is soluble in acids and solutions of alkali hydroxides and carbonates. It decomposes at about 250° and has a sp. gr. 2.82 at 16° . With a dilute solution of ferric chloride, it slowly gives a green coloration passing into blue. The *ammonium*, *potassium*, and *sodium* salts are crystalline. The *anilide*, prepared by boiling the acid with aniline, is a greyish-brown powder which is soluble in alkalis and acids, but insoluble in neutral solvents, and is not converted into the aniline salt by prolonged ebullition with water. It decomposes at about 190° and has a sp. gr. 3.19 at 17° . T. A. H.

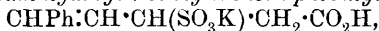
Crystalline Form of Optically Active Substances, particularly of a Partially Racemic Active Compound. FEDERICO MILLOSEVICH (*Atti R. Accad. Lincei*, 1904, [v], 13, 78—85).—The following compounds were obtained by Andreocci (Abstr., 1899, i, 931).

d- and *l*-Acetyl-desmotroposantonin, having respectively $[\alpha]_D + 122.6^\circ$ and -122.9° , crystallise in enantiomorphous, hemihedral, orthorhombic forms $[a:b:c = 0.6984:1:0.9482]$; the racemic mixture of these two, melting at 145° , is probably anorthic, but cannot be obtained in measurable crystals. The active, partially-racemic mixture, melting at 142° , of the *l*-acetyl derivative melting at 154° , and the *d*-acetyl derivative melting at 156° (*loc. cit.*), forms hemimorphic, monoclinic crystals $[a:b:c = 1.5954:1:0.8602; \beta = 79^\circ 30']$; its peculiarities have already been noted. The *d*-acetyl derivative melting at 156° is probably orthorhombic.

Of the foregoing compounds, those melting at 156° and at 142° show triboluminescence (compare Andreocci, Abstr., 1899, ii, 719); these are the forms which also have an excellent cleavage. W. A. D.

Addition of Acid Sulphites to Cinnamylidenemalonic Acid. ELMER P. KOHLER (*Amer. Chem. J.*, 1904, 31, 243—256).—When an aqueous solution containing molecular proportions of potassium hydrogen sulphite and cinnamylidenemalonic acid is left in the cold for 4 or 5 days, the potassium salts of benzylidenesulphoethylmalonic and benzylidenesulphobutyric acids are produced, and may be separated by means of a strong solution of potassium hydroxide, in which the

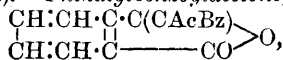
salt of the former acid is but sparingly soluble. *Potassium benzylidenesulphoethylmalonate*, $\text{CHPh}:\text{CH}:\text{CH}(\text{SO}_3\text{K})\cdot\text{CH}(\text{CO}_2\text{K})_2$, prepared by gradually adding potassium hydrogen sulphite to a hot solution of potassium cinnamylidenemalonate and pouring the product into cold solution of potassium hydroxide, crystallises in white, lustrous plates and readily suffers decomposition. If its aqueous solution is boiled for a few hours and then acidified, cinnamylidenemalonate acid is precipitated. When dilute hydrochloric acid is added to a boiling solution of the salt, *potassium hydrogen benzylidenesulphobutyrate*,



is produced, which crystallises in plates; it can be prepared more readily by the gradual addition of potassium sulphite to finely-powdered cinnamylidenemalonate acid suspended in boiling water; when heated with concentrated hydrochloric acid or with alkalis, it is converted into cinnamylacetic acid. *Benzylidenesulphobutyric acid* crystallises in colourless needles, melts at 76° , decomposes at $125\text{--}130^\circ$, and is readily soluble in water, alcohol, or acetone; its normal *potassium*, *calcium*, and *barium* salts are described. When this acid is oxidised with potassium permanganate in neutral or alkaline solution, benzoic, malic, and sulphuric acids are formed, but in a solution acidified with phosphoric acid, benzaldehyde, benzoic acid, carbon dioxide, and β -sulphopropionic acid are produced. When bromine is added to a solution of the acid, a blood-red, amorphous precipitate is produced which, if left in contact with the liquid, rapidly becomes colourless; the liquid becomes milky and afterwards clear, and a colourless substance, $\text{C}_{11}\text{H}_{11}\text{O}_5\text{SBr}$, which appears to be a sultonic acid, separates in small, lustrous crystals; its *methyl* ester crystallises in large, colourless prisms and melts at 148° ; the *ethyl* ester melts at 121° . E. G.

Preparation and Properties of Phthalylbenzoylacetone.

CARL BÜLOW and BERTHOLD KOCH (*Ber.*, 1904, 37, 577—588. Compare *Abstr.*, 1887, 141).—*Phthalylbenzoylacetone*,

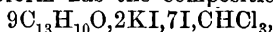


obtained by the action of phthalyl chloride on sodiobenzoylacetone suspended in dry ether, crystallises from boiling alcohol in colourless, hexagonal plates melting at 175° . The *bisphenylhydrazone*, $\text{C}_{30}\text{H}_{24}\text{O}_2\text{N}_4$, melts at 181° , is only sparingly soluble in ether, and dissolves in pure sulphuric acid to a colourless solution which gives the Bülow reaction. The *bis-p-nitrophenylhydrazone* crystallises from acetic acid in pale yellow needles melting at 243° , and dissolves in both dilute sodium hydroxide solution and concentrated sulphuric acid. The *bis-p-bromophenylhydrazone* crystallises in flat, yellow needles melting at 201° , the *bis-semicarbazone*, $\text{C}_{20}\text{H}_{18}\text{O}_4\text{N}_6$, forms glistening, colourless needles, melts at 252° , and dissolves in alcohol, acetic acid, sodium hydroxide solution, and concentrated sulphuric acid. The *dioxime* crystallises in colourless, glistening plates, melts at 63° , and has an odour of camphor.

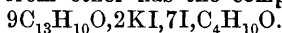
Hydrolysis with water converts phthalylbenzoylacetone into phthalic acid, benzoylacetone, acetophenone, and acetic acid. Cold alcoholic ammonia transforms the phthalyl derivative into phthal-

amide, benzoylacetone, and benzoylacetanamine (Abstr., 1885, 1237). On reduction with zinc dust and acetic acid, it yields *phthalidylbenzoylacetone*, $C_6H_4 \left\langle \begin{array}{c} CH(CHAcBz) \\ CO \end{array} \right\rangle O$, which crystallises from hot acetic acid in colourless needles, melting at 119° , and is insoluble in dilute sodium carbonate. With an acetic acid solution of *p*-nitrophenylhydrazine, it yields *5-phenyl-1-p-nitrophenyl-4-phthalidyl-3-methylpyrazole* in the form of reddish-brown crystals melting at 169° . A second reduction product of phthalylbenzoylacetone is *benzoylacetonebenzyl-o-carboxylic acid*, $COMe \cdot CHBz \cdot CH_2 \cdot C_6H_4 \cdot CO_2H$, which crystallises from alcohol in small, colourless needles melting at 136° . With *p*-nitrophenylhydrazine, this yields *5-phenyl-1-p-nitrophenyl-4-carboxybenzyl-3-methylpyrazole* in the form of orange-red needles melting at 219° , and with hydroxylamine hydrochloride and sodium acetate, *5-phenyl-4-o-carboxybenzyl-3-methylisooxazole* melting at $189-190^\circ$.
J. J. S.

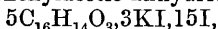
Addition of Iodine and Potassium Iodide to Organic Compounds containing the Carbonyl Group. ALPHONSO M. CLOVER (*Amer. Chem. J.*, 1904, 31, 256-268).—When a mixture of iodine (4 parts), potassium iodide (3 parts), and benzophenone (8 parts) is heated for a few minutes at 100° , a crystalline product with a golden lustre is obtained. If this substance is recrystallised from chloroform or ether, hexagonal prisms are produced, the sides of which have a golden lustre whilst the bases are dark blue. The compound melts at about 100° and is very soluble in ethyl acetate, acetic acid, or acetone. In dilute solution, it undergoes dissociation into its constituents. When it is shaken with benzene, the iodine and benzophenone are gradually dissolved and the potassium iodide remains as a residue. If the compound is shaken with water, the iodine and potassium iodide slowly pass into solution and the benzophenone is left undissolved. The compound crystallised from chloroform has the composition



and that crystallised from ether has the composition



Benzoic anhydride yields a similar compound, $12C_{14}H_{10}O_3, 4KI, 11I$, which melts at $125-128^\circ$. Phthalic anhydride furnishes the compound, $2C_8H_4O_3, KI, 4I$, which forms dark green, lustrous crystals of irregular shape. With phenylacetic anhydride, the compound,



is obtained. The succinic anhydride compound, $4C_4H_4O_3, KI, 2I$, forms a golden, crystalline mass.

Similar compounds are formed with benzanilide, nitrobenzoyl chloride, and methyl oxalate. Evidence was also obtained of the formation of compounds with acetone and acetic anhydride, but with ethers, alcohols, and phenols no such substances appear to be formed.

E. G.

Disulphones. XIII. Sulphur Derivatives of Unsaturated Ketones. THEODOR POSNER (*Ber.*, 1904, 37, 502-510. Compare Abstr., 1899, i, 604; 1900, i, 5, 16; 1901, i, 14, 88, 474, 703; 1902, i, 82, 220, 296, 622; 1903, i, 242).—In a previous communication (Abstr., 1902, i, 296), the action of mercaptans on unsaturated ketones

was studied, and the influence of the double linking in various ketones on the reactivity of the latter with mercaptans particularly observed. The property possessed by these unsaturated ketones of forming sulphones is now shown to be conditioned, not by the proximity of the ketonic group, but by the presence of the double linkings. The normal ketone reaction becomes less marked with the introduction of alkyl or phenyl groups into the molecule of the unsaturated ketone. Whereas benzylideneacetone, $\text{CHPh}:\text{CH}\cdot\text{COMe}$, reacts with all mercaptans, dypnone, $\text{CMePh}:\text{CH}\cdot\text{COPh}$, and benzylideneacetophenone, $\text{CHPh}:\text{CH}\cdot\text{COPh}$, react with ethyl mercaptan only, and benzaldehydobenzoin, $\text{CHPh}:\text{CPh}\cdot\text{COPh}$, does not react at all with mercaptans.

The results are also discussed in the light of Thiele's theory of partial valencies.

βδδ-Triethylsulphonepentane (ethylideneacetone triethylsulphone),



prepared from ethylideneacetone and ethyl mercaptan, separates from alcohol in glistening, rhombic leaflets and melts at 106° .

βδδ-Tribenzylsulphonepentane (ethylideneacetone tribenzylsulphone),

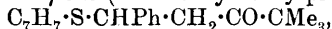


prepared from ethylideneacetone and benzyl mercaptan, separates from alcohol as a crystalline powder and melts at $187\text{--}188^\circ$.

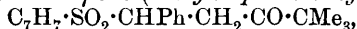
αβγ-Triphenyl-α-ethylsulphonepropane-γ-one (ethylsulphonebenzyldeoxybenzoin), $\text{SO}_2\text{Et}\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{COPh}$, prepared by oxidising αβγ-triphenyl-α-thiolethylpropane-γ-one (thiolethylbenzyldeoxybenzoin) in acetic acid solution, separates from alcohol in glistening, colourless needles and melts at $206\text{--}207^\circ$.

αβγ-Triphenyl-α-thiolbenzylpropane-γ-one (thiolbenzylbenzyldeoxybenzoin), $\text{C}_7\text{H}_7\text{S}\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{COPh}$, prepared from benzyl mercaptan and benzylidenedeoxybenzoin, crystallises from alcohol in needles and melts at 207° . Its chloroform solution, when oxidised, yields αβγ-triphenyl-α-benzylsulphonepropane-γ-one (benzylsulphonebenzyldeoxybenzoin), $\text{C}_7\text{H}_7\cdot\text{SO}_2\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{COPh}$, which separates from glacial acetic acid in needles and melts at $252\text{--}254^\circ$.

α-Phenyl-α-ethylsulphone-δ-dimethylpentane-γ-one (ethylsulphonebenzylpinacolin), $\text{SO}_2\text{Et}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CMe}_3$, prepared by oxidising the oil obtained by interaction of benzylidenepinacolin and ethyl mercaptan, melts at $122\text{--}124^\circ$, and, with benzyl mercaptan, forms α-phenyl-α-thiolbenzyl-δ-dimethylpentane-γ-one (thiolbenzylbenzylpinacolin),



which crystallises from alcohol in rhombic prisms and melts at $62\text{--}63^\circ$. The latter compound yields, on oxidation, α-phenyl-α-benzylsulphone-δ-dimethylpentane-γ-one (benzylsulphonebenzylpinacolin),

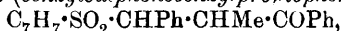


which separates from alcohol in needles and melts at $133\text{--}134^\circ$.

α-Phenyl-α-thiolphenyl-δ-dimethylpentane-γ-one (thiolphenylbenzylpinacolin), $\text{SPh}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CMe}_3$, prepared from benzylidenepinacolin and thiophenol, separates from alcohol in silky needles and melts at $86\text{--}88^\circ$.

α-Phenyl-α-phenylsulphone-δ-dimethylpentane-γ-one (phenylsulphonebenzylpinacolin), $\text{SO}_2\text{Ph}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CMe}_3$, separates from alcohol as a white powder and melts at $161\text{--}164^\circ$.

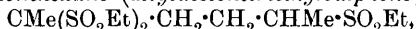
The oil, obtained by interaction of benzylidenepropiophenone and benzyl mercaptan, yielded, on oxidation, *α*-benzylsulphone-*αγ*-diphenyl-*β*-methylpropane-*γ*-one (benzylsulphonebenzylpropiophenone),



which crystallises from alcohol in glistening, rhombic prisms and melts at 152—153°.

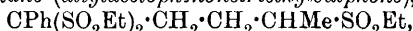
The condensation product obtained from allyl acetone and benzyl mercaptan yielded, on oxidation, *ββ*-tribenzylsulphonehexane (allylacetone-tribenzylsulphone), $\text{CMe}(\text{SO}_2 \cdot \text{C}_7\text{H}_7)_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{SO}_2 \cdot \text{C}_7\text{H}_7$, which separates from alcohol in needles and melts at 129—130°.

ββ-Triethylsulphonehexane (allylacetone-triethylsulphone),



prepared in an analogous manner, crystallises from alcohol in colourless leaflets and melts at 125—130°.

Allylacetophenone, in an analogous manner, yielded *α*-phenyl-*αα*-triethylsulphonepentane (allylacetophenone-triethylsulphone),



which melts at 163°.

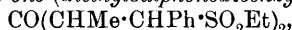
α-Phenyl-*αα*-tribenzylsulphonepentane (allylacetophenone-tribenzylsulphone), $\text{CPh}(\text{SO}_2 \cdot \text{C}_7\text{H}_7)_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{SO}_2 \cdot \text{C}_7\text{H}_7$, melts at 225°.

Methylheptenone yielded the two sulphones, *β*-methyl-*βζζ*-triethylsulphoneheptane (methylheptenone-triethylsulphone),



and *β*-methyl-*βζζ*-tribenzylsulphoneheptane (methylheptenone-tribenzylsulphone), $\text{C}_7\text{H}_7 \cdot \text{SO}_2 \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe}(\text{SO}_2 \cdot \text{C}_7\text{H}_7)$, which separates from alcohol in needles and melts at 158°.

Dibenzylidenediethyl ketone yielded *α*-diphenyl-*α*-diethylsulphone-*βδ*-dimethylpentane-*γ*-one (diethylsulphonedibenzylidiethyl ketone),



and *α*-diphenyl-*α*-dibenzylsulphone-*βδ*-dimethylpentane-*γ*-one (dibenzylsulphonedibenzylidiethyl ketone),



which separates from alcohol in needles, grouped in rosettes, and melts at 209—210°.

The oil, obtained by the condensation of cinnamylideneacetone with mercaptan, yielded on oxidation *α*-phenyl-*αγ*-diethylsulphonehexane-*γ*-one (diethylsulphonephenylbutyl methyl ketone),



α-Phenyl-*αγ*-dibenzylsulphonehexane-*ε*-one (dibenzylsulphonephenylbutyl methyl ketone), $\text{C}_7\text{H}_7 \cdot \text{SO}_2 \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CH}(\text{SO}_2 \cdot \text{C}_7\text{H}_7) \cdot \text{CH}_2 \cdot \text{COMe}$, separates from glacial acetic acid in needles and melts at 265°.

α-Phenyl-*αγ*-diphenylsulphonehexane-*γ*-one (diphenylsulphonephenylbutyl methyl ketone), $\text{SO}_2 \text{Ph} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CH}(\text{SO}_2 \text{Ph}) \cdot \text{CH}_2 \cdot \text{COMe}$, separates from alcohol in slender needles and melts at 107—109°.

αγ-Ethylsulphone-*α*-diphenylpentane-*ε*-one (diethylsulphonephenylbutyl phenyl ketone), $\text{SO}_2 \text{Et} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CH}(\text{SO}_2 \text{Et}) \cdot \text{CH}_2 \cdot \text{COPh}$, is a viscous oil.

αγ-Dibenzylsulphone-*α*-diphenylpentane-*ε*-one (dibenzylsulphonephenylbutyl phenyl ketone),



was also prepared.

α-Dithio-phenyl-*α*-diphenylpentane-*ε*-one (dithiolphenylphenylbutyl phenyl ketone), $\text{SPh} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CH}(\text{SPh}) \cdot \text{CH}_2 \cdot \text{COPh}$, melts at 102° .

A. McK.

Preparation of *o*-Nitrophenyllactoketone [*o*-Nitro-*α*-hydroxybenzylacetone]. SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE ANCT. GILLIAD, P. MONNET, & CARTIER (D.R.-P. 146294).—*o*-Nitrobenzaldehyde condenses with acetone in presence of alkaline compounds, such as sodium sulphite or trisodium phosphate, the reaction taking place at the ordinary temperature or when cooled by ice. A purer product and better yield are obtained than by employing alkali hydroxides as the condensing agent.

C. H. D.

Phenylbenzoquinone [Diphenylquinone] and Derivatives of Diphenyl. FRITZ FICHTER and AUGUST SULZBERGER (*Ber.*, 1904, 37, 878—884. Compare Borsche, *Abstr.*, 1900, i, 25, 594; H. B. Hill, *ibid.*, 392).—*o*-Aminodiphenyl (Huebner, *Annalen*, 1881, 209, 349) may readily be obtained by reducing the corresponding nitro-derivative with stannous chloride and concentrated hydrochloric acid; on oxidation with manganese dioxide and sulphuric acid, it gives an 11 per cent. yield of diphenylquinone melting at 114° . The corresponding diphenylquinhydrone melts at 177° .

3-Nitro-4-acetylaminodiphenyl is readily obtained by the action of fuming nitric acid on an acetic acid solution of *p*-acetylaminodiphenyl; it crystallises from alcohol in yellow needles melting at 132° , and, on reduction with tin and hydrochloric acid, yields 5-phenyl-2-methylbenziminazole, $\text{C}_6\text{H}_3\text{Ph} \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{CMe}$, in the form of colourless plates melting at 116° .

3-Nitro-4-aminodiphenyl, obtained by the hydrolysis of the acetyl derivative with alcoholic potash, crystallises in red needles melting at 167° , and, on treatment with sulphuric acid and ethyl nitrite, yields 3-nitrodiphenyl melting at 58.5° ; Jacobson and Loeb (*Ber.*, 1903, 36, 4082) give 61° .

3-Acetylaminodiphenyl melts at 148° .

3:5-Dinitro-4-acetylaminodiphenyl, obtained as a by-product in the preparation of the mononitro-derivative, crystallises from acetic acid or nitrobenzene in pale yellow needles melting at $240\text{--}241^\circ$; when reduced with tin and hydrochloric acid, it yields 7-amino-5-phenyl-2-methylbenziminazole, $\text{NH}_2 \cdot \text{C}_6\text{H}_2\text{Ph} \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{CMe}$, melting at 94° .

3:5-Dinitro-4-aminodiphenyl crystallises from alcohol in orange-yellow needles melting at 233° .

J. J. S.

Halogen Derivatives of Tertiary Bases of the Anthraquinone Series. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 146691).—Tertiary dialkylaminoanthraquinones (*Abstr.*, 1903, i, 498) react with halogens without removal of the alkyl groups. In presence of an excess of halogen, additive compounds may also be formed.

A solution of *α*-dimethylaminoanthraquinone in hydrochloric acid reacts with bromine (4 atoms) forming a yellow, crystalline *perbromide*,

from which 2 atoms of bromine may be removed by ammonia or sodium hydrogen sulphite, forming 1-bromo-4-dimethylaminoanthraquinone; this crystallises from pyridine or methyl alcohol in garnet-red leaflets and melts at 178°, and forms crystalline salts with acids. If only 2 atoms of bromine are employed, one-half of the original compound is converted into the perbromide, which reacts on warming to 80° with the remaining unaltered base, forming the bromo-derivative. 4:8-Dibromo-1:5-tetramethyldiaminoanthraquinone, from 1:5-tetramethyldiaminoanthraquinone, crystallises from pyridine in orange-red leaflets with green reflex, melts at 236°, and forms colourless salts with acids. Excess of bromine forms a crystalline perbromide. Bromo-1-nitro-8-dimethylaminoanthraquinone crystallises from pyridine in brown, glistening needles and melts at 198°. Its salts are decomposed by water. Bromodimethylaminoanthraquinone-1-sulphonic acid is sparingly soluble in water, and is less basic than the unbrominated acid. 1-Chloro-4-dimethylaminoanthraquinone, prepared by the action of hydrochloric acid and potassium chlorate on 1-dimethylaminoanthraquinone, melts at 172° (compare *loc. cit.*). C. H. D.

Compounds of Anthraquinone with Aromatic Amines. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 148079).—Anthraquinone condenses with aromatic amines, forming compounds in which the ketonic oxygen is probably replaced by the aminic residue. Thus, when anthraquinone is heated with *p*-toluidine and boric acid, a compound is obtained, which dissolves in cold, concentrated sulphuric acid to a colourless solution with blue fluorescence, and crystallises from pyridine in golden leaflets or thick, glistening crystals containing pyridine. Anthraquinone and aniline form a mixture of two compounds, one of which, forming thick crystals, is converted on further heating with aniline into the second compound, which dissolves in concentrated sulphuric acid, the solution becoming blue, and then green with an intense blue fluorescence, on warming. C. H. D.

Anthraquinone-1-sulphonic Acid. MAX DÜNSCHMANN (*Ber.*, 1904, 37, 331—333. Compare Iljinsky, this vol., i, 176, and Schmidt, *ibid.*, i, 256).—It is shown that anthraquinone-1-sulphonic acid is always formed in small quantities in the normal sulphonation of anthraquinone; details are given for separating it from its congeners by taking advantage of the greater solubility of its sodium salt compared with that of the sodium 2-sulphonate and 2:6-disulphonate in strongly alkaline solution at 50—55°. W. A. D.

Anthraquinone-1-sulphonic Acid. CARL LIEBERMANN and BERNHARD PLEUS (*Ber.*, 1904, 37, 646—648).—In connection with Dünschmann's (preceding abstract) recent discovery that commercial anthraquinone-2-sulphonic acid also contains small quantities of the 1-sulphonic acid, it is pointed out that Liebermann and Bischof (*Abstr.*, 1880, 399) had previously obtained small quantities of the barium salt of anthracenecarboxylic acid melting at 245°, which was presumably derived from anthraquinone-1-sulphonic acid present in the commercial

product. It is now shown that this barium salt is easily prepared from the pure anthraquinone-1-sulphonic acid. E. F. A.

Oxidation Products of Quinizarin. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 146223).—Quinizarin is oxidised by heating under pressure with solutions of sodium carbonate, phosphate, borate, acetate, &c., at 120° , forming a mixture of an oxidation product and its leuco-base. The ketonic group appears to exert an oxidising action, being itself reduced. The leuco-compound is converted into the blue oxidation product by boiling its solution with sodium hydroxide. A soluble and an insoluble compound are obtained, the latter predominating at higher temperatures. The insoluble sodium salt may be filtered off and decomposed by acids, forming a *compound*, $C_{28}H_{12}O_8$, which crystallises from quinoline in yellowish-red needles and dissolves in sulphuric acid to a bluish-violet solution. The bluish-violet alkali salts are sparingly soluble in water. On acidifying the filtrate from the sodium salt, a *compound*, $C_{28}H_{14}O_8$, is precipitated, which crystallises from nitrobenzene in long, orange needles, dissolving in sulphuric acid to a reddish-violet solution, and in alkali hydroxides to blue solutions. Both compounds are very sparingly soluble in organic solvents, and their aqueous solutions show characteristic spectra on the addition of boric acid. C. H. D.

Derivatives of Menthylxanthic Acid and Menthenes from Different Sources. L. A. TSCHUGAEFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 1116—1179).—*Methyl menthylxanthate*, $C_{10}H_{19}O \cdot CS_2Me$, obtained by the action of methyl iodide or sulphate on sodium menthylxanthate, crystallises from alcohol in almost colourless, slender needles, or from a mixture of ether and alcohol in large prisms melting at 39° ; it is readily soluble in ether, benzene, toluene, or chloroform, slightly so in methyl or ethyl alcohol, and has the normal molecular weight in freezing benzene or acetic acid, and $[\alpha]_D - 79.47^{\circ}$ in benzene, -80.02° in ethyl acetate, and -80.72° in chloroform. On dry distillation, it is decomposed according to the equation: $C_{10}H_{19}O \cdot CS_2Me = C_{10}H_{18} + CSO + SHMe$.

The *menthene* thus obtained boils at 167.9° under 751 mm. pressure, has $[\alpha]_D + 116.74^{\circ}$, sp. gr. 0.8122 at $20^{\circ}/4^{\circ}$, and $n_D 1.45242$ at 20° , this value giving the normal molecular refraction for a compound with one ethylene linking; it exhibits normal cryoscopic behaviour in benzene. Its *nitrosochloride*, $C_{10}H_{18} \cdot NOCl$, crystallises from a mixture of chloroform and methyl alcohol in thin, colourless needles, and melts at 111 — 112° when very slowly heated, or as high as 127° when quickly heated; it is readily soluble in chloroform, and, to a slight extent, in benzene, toluene, or ether, but practically insoluble in solvents containing hydroxyl; it has $[\alpha]_D + 230.1^{\circ}$ in benzene, $+192.3^{\circ}$ in chloroform, and $+183.1^{\circ}$ in ethyl acetate.

Ethyl menthylxanthate, $C_{10}H_{19}O \cdot CS_2Et$, prepared from the corresponding sodium salt and ethyl iodide, is obtained as a pale yellow, viscous liquid, which solidifies, on cooling, to a crystalline mass melting at about 9° ; it is readily soluble in ether, benzene, toluene, or chloro-

form, and slightly so in methyl or ethyl alcohol; it has the normal molecular weight in freezing benzene, a sp. gr. 1.0192 at 21°/4°, $[\alpha]_D - 60.10^\circ$, and $n_D 1.52761$ at 21°. It decomposes, on heating, in a similar manner to the methyl derivative, and the menthene obtained boils at 167.4—167.8° under 750 mm. pressure and has the following constants: sp. gr. at 20°/4°, 0.8120, $[\alpha]_D + 116.16^\circ$, $n_D = 1.45227$ at 20°.

Menthylidixanthide, $S_2(CS \cdot O \cdot C_{10}H_{19})_2$, prepared by the action of iodine on sodium menthylxanthate, separates from a mixture of toluene and ethyl acetate in yellow, rhombic crystals $[a:b:c = 0.7207:1:1.2788]$ melting at 92.5—93°; it is readily soluble in benzene, toluene, chloroform, or ether, has the normal molecular weight in freezing benzene, $[\alpha]_D - 231.4^\circ$ in benzene, -286.10° in toluene, -286.88° in chloroform, and -289.44° in ethyl acetate. A menthylidixanthide with similar properties is obtained by the action of copper sulphate on sodium menthylxanthate. On distillation, menthylidixanthide yields hydrogen sulphide, carbon oxysulphide, menthene, and menthol. The mode of decomposition is hence quite different from that of diethylxanthide (see Debus, *Annalen*, 1853, 72, 4, and 1854, 75, 122).

Menthylxanthic thioanhydride, $(C_{10}H_{19}O \cdot CS)_2S$, prepared by the interaction of methyl or ethyl chlorocarbonate and sodium menthylxanthate, $2C_{10}H_{19}O \cdot CS_2Na + OR \cdot COCl = (C_{10}H_{19}O \cdot CS)_2S + OR \cdot COSNa + NaCl$, separates from a mixture of benzene and alcohol in greenish-yellow, slender crystals or from a mixture of ether and benzene in large, rectangular plates melting at 148—149°; the crystals belong to the rhombic system, and are apparently sphenoidally hemihedral $[a:b:c = 1.4469:1:1.4708]$; it is readily soluble in ether, benzene, toluene, and chloroform, and, to a less extent, in alcohol, and it exhibits normal cryoscopic behaviour in freezing benzene; $[\alpha]_D$ in benzene solution has the value -53.79° .

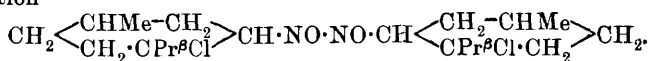
When heated together, sodium menthylxanthate and benzoyl chloride react according to the equations, $2C_{10}H_{19}O \cdot CS_2Na + CPhCl = (C_{10}H_{19}O \cdot CS)_2S + CPh \cdot SNa + NaCl$ and $CPhCl + CPh \cdot SNa = NaCl + (CPh)_2S$. Menthylxanthic thioanhydride, when heated, decomposes thus: $(C_{10}H_{19}O \cdot CS)_2S = C_{10}H_{18} + C_{10}H_{19} \cdot OH + COS + CS_2$.

Menthylxanthamide, $C_{10}H_{19}O \cdot CS \cdot NH_2$, prepared by the action of alcoholic ammonia on menthylidixanthide or on menthylxanthic thioanhydride or, best of all, on methyl menthylxanthate, separates from a mixture of benzene and light petroleum in slender needles, or on slow cooling, or from a mixture of alcohol and ether, in large, monoclinic prisms melting at 144—145°, and dissolving readily in alcohol, benzene, ether, or chloroform, and very slightly in light petroleum; in the dark, the crystals exhibit triboluminescence. It has the normal molecular weight in freezing acetic acid or benzene, and $[\alpha]_D - 120.78^\circ$ in benzene, -121.58° in toluene, -115.90° in ethyl acetate, -110.99° in dimethylaniline, and -113.17° in alcohol. On heating with alcoholic potassium hydroxide, menthylxanthamide is decomposed according to the equation: $C_{10}H_{19}O \cdot CS \cdot NH_2 + KOH = C_{10}H_{19} \cdot OH + KSCN + H_2O$; this is similar to the hydrolysis of ethylxanthamide (Debus, *loc. cit.*). On heating, menthylxanthamide decomposes, thus: $C_{10}H_{19}O \cdot CS \cdot NH_2 =$

$C_{10}H_{18} + NH_3 + CSO$, whilst ethylxanthamide yields ethyl mercaptan, and cyanic and cyanuric acids: $OEt \cdot CS \cdot NH_2 = SHEt + CHON$.

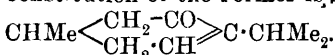
When heated, $\alpha\beta$ -diphenyl- γ -*l*-menthyliminoxanthide is resolved according to the equation: $NPh \cdot CPh \cdot S \cdot CS \cdot O \cdot C_{10}H_{19} = SH \cdot CPh \cdot NPh + COS + C_{10}H_{18}$. The menthene thus obtained possesses approximately the same properties as menthenes prepared by other modifications of the xanthic method. The author concludes that this menthene is an individual compound, and is obtained from menthol without isomeric change taking place.

Menthene nitrosochloride possesses double the normal molecular weight in freezing benzene, and the author ascribes to it the constitution



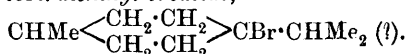
On heating menthene nitrosochloride, it loses a molecule of hydrogen chloride and yields nitrosomenthene, the ketone, of which this is the oxime, being obtained by heating with dilute hydrochloric acid; this ketone, menthenone, gives menthol on reduction. It is hence possible to start from menthol, and, passing successively through menthyl-xanthic ester, menthene, menthene nitrosochloride, nitrosomenthene, and menthenone, to obtain again the original menthol.

On comparing menthenone with pulegone, it will be seen that the constitution of the former is probably to be represented by the formula



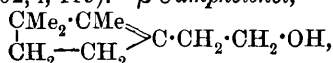
When reduced by means of sodium in alcoholic solution, menthene nitrosochloride yields *l*-menthylamine.

Menthene obtained by the xanthic method gives, with hydrogen bromide, mainly *tert*-menthyl bromide,



The relationship existing between the various menthol derivatives is discussed and the following conclusions, in addition to those already given, are drawn: (1) the different xanthic derivatives of menthol are capable of decomposing readily at high temperatures, yielding one and the same menthene, possessing high optical activity. (2) All attempts to discover non-homogeneity in this menthene are fruitless. (3) The menthenes obtained from *l*-menthol by means of halogen hydracids consist mainly of *d*- Δ^3 -menthene, giving *d*-nitrosochlorides. (4) The menthenes obtained from *l*-menthol by means of acid dehydrating agents contain little Δ^3 -menthene, but consist mainly of an isomeride in which the double linking has a different position. T. H. P.

An Isomeride of Borneol, β -Campholenol, and some Derivatives. AUGUSTE BÉHAL (*Compt. rend.*, 1904, 138, 280—282. Compare Abstr., 1902, i, 419).— *β -Campholenol*,



produced by reducing inactive ethyl campholate with sodium and alcohol (compare Bouveault and Blanc, Abstr., 1903, i, 597, 673, 730), is a liquid with a faint odour of camphor, boiling at 215—216° under

760 mm. pressure; it has a sp. gr. 0.9231 at 0° and 0.9096 at 20°, and n_D 1.47101 at 20°. *Campholenyl formate*, prepared by the action of acetic and formic anhydrides on the alcohol, boils at 215—216°, and has a sp. gr. 0.9800 at 0° and 0.9718 at 20°, and n_D 1.45742 at 20°. *Campholenyl acetate* boils at 228—229°, and has a sp. gr. 0.9518 at 0° and 0.9355 at 20°, and n_D 1.45562 at 22°. *Campholenyl butyrate* boils at 252—254° and has a sp. gr. 0.9660 at 0° and 0.9581 at 20°.

When β -campholenol is boiled with dilute sulphuric acid, it is converted into an isomeric internal ether, campholan oxide, $C_{10}H_{18}O$, which boils at 180—182°, has a sp. gr. 0.9303 at 0° and 0.9173 at 19°, and n_D 1.46071 at 19°. The mechanism of the reaction whereby this compound is formed from the alcohol appears to be (1) the breaking down of the ethylenic union by the fixation of the elements of a molecule of water, (2) the dehydration of the γ -glycol thus produced, for this com-

pound, β -campholan- $\alpha\beta$ -diol, $CH_2 \begin{smallmatrix} \text{CMe}_2 \cdot \text{CMe}(\text{OH}) \\ \text{CH}_2 - \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2\text{OH} \end{smallmatrix}$, prepared by reducing inactive campholenolactone by Bouveault and Blanc's method, is crystalline, melts at 145°, is slightly soluble in light petroleum, soluble in alcohol or benzene, and yields *campholan oxide*,

$CH_2 \begin{smallmatrix} \text{CMe}_2 \cdot \text{CMe} - \text{O} \\ \text{CH}_2 - \text{CH} \cdot \text{CH}_2 \end{smallmatrix} \text{CH}_2$, on boiling with dilute sulphuric acid.

β -Campholan- $\alpha\beta$ -diol can also be obtained by the hydrogenation of dehydrocampholenolactone, $CH_2 \begin{smallmatrix} \text{CMe}_2 \cdot \text{CMe} \cdot \text{O} \\ \text{CH}_2 - \text{C} = \text{CH} \end{smallmatrix} \text{CO}$, or ethyl keto-

campholenate, $CH_2 \begin{smallmatrix} \text{CMe}_2 \cdot \text{CMe} \\ \text{CH}_2 - \text{C}(\text{CH}_2 \cdot \text{CO}_2\text{Et}) \end{smallmatrix} \text{O}$.

M. A. W.

Constitution of Camphor. GIUSEPPE ODDO (*Ber.*, 1904, 37, 511—515).—A claim for priority. The author points out that he was the first to indicate the possibility of formulating camphor with two alicyclic rings, united to one another in a position different from the ortho-position. At the time when the author's formula for camphor was submitted (1891), it sufficed to account satisfactorily for the relationships between camphor and the camphor derivatives then known.

A. McK.

Ethylidenecamphor. Ethylhomocamphoric Acid. JULES MINGUIN (*Compt. rend.*, 1904, 138, 577—579).—Ethylcamphor is prepared from methyl ethylcamphocarboxylic acid by heating at 180—200° with alcoholic potash; it boils at 107—110° under 10 mm. pressure and has $[\alpha]_D + 40^\circ$ in alcoholic solution. Bromination of ethylcamphor in carbon disulphide solution yields *monobromoethylcamphor*, a liquid which boils and partially decomposes at 115—120° under 10 mm. pressure. When boiled with alcoholic potash, this yields *ethylidenecamphor*, $C_8H_{14} \begin{smallmatrix} \text{C} \cdot \text{CHMe} \\ \text{CO} \end{smallmatrix}$, as a liquid which boils at 110—115°

under 10 mm. pressure, and has $[\alpha]_D + 113^\circ$ in alcoholic solution. The rotatory power of ethylidenecamphor is therefore considerably greater than that of ethylcamphor, a relation which has already been recorded in the case of methylcamphor and methylenecamphor (Abstr.,

1903, i, 428). During the preparation of ethylcamphor from the methyl ethylcamphocarboxylate, a certain amount of ethyl- β -homocamphoric acid is formed. The substance is soluble in ether, melts at 135—140°, and has $[\alpha]_D + 39.65^\circ$ in alcoholic solution. S. S.

Essential Oil of Boldo. E. TARDY (*J. Pharm. Chim.*, 1904, [vi], 19, 132—136).—Dried leaves of *Boldoa fragrans* yield rather less than 2 per cent. of essential oil, of a greenish-yellow colour, having the sp. gr. 0.876 at 15° and $n_D - 6.30$ in a 10 cm. tube. The oil contains small proportions of eugenol, cumic aldehyde, and acetic esters. By distillation, the presence of a dextrorotatory and of a levorotatory terpene, the latter in considerable amount, and of an inactive terpineol was proved. A levorotatory sesquiterpene was also obtained, which was, however, probably produced during the distillation. G. D. L.

South American Orange Oil. JOHN C. UMNEY and CHARLES T. BENNETT (*Pharm. J.*, 1904, [iv], 18, 217—218).—An account is given of an orange oil of unknown origin imported from Buenos Ayres. The characters of this oil resembled those of orange-leaf oil more closely than those of orange-flower oil, and it contained only traces of methyl-anthranilate. It had a sp. gr. 0.887 and $n_D + 2^\circ$. It contained 36.5 per cent. of esters (calculated as linaloyl acetate) and 38.4 per cent. of free alcohols (calculated as geraniol), or total alcohols 67.1 per cent. On distillation under atmospheric pressure, it yielded 5 per cent. below 190°, 12 per cent. below 195°, 25 per cent. below 200°, 35 per cent. below 205°, 54 per cent. below 210°, 65 per cent. below 215°, 80 per cent. below 220°, and 20 per cent. above 220°. The sp. gr., n_D , and n_D are given of each of the various fractions obtained by distillation under reduced pressure. The oil was found to contain pinene, dipentene, linalool, geraniol, and furfuraldehyde. E. G.

Constitution of Gutta-percha Resin. CARL O. WEBER (*Chem. Centr.*, 1904, i, 517—518; from *Gummi-Zeit.*, 18, 342—343. Compare *Abstr.*, 1902, i, 552).—It is very doubtful whether the constitution of gutta-percha resin is represented by Tschirch's formula (this vol., i, 76) which contains hexane rings, since gutta-percha itself, like caoutchouc, is a polyterpene and has an open carbon chain. The hexane formula does not really represent an oxypolyterpene, but a condensation product of a terpene alcohol of the type of an ether. The complex molecule of gutta-percha or caoutchouc is doubtless split up on oxidation, but there is no evidence to show that the disintegration is as thorough as Tschirch's formula would imply.

The nature of the products formed by the oxidation of gutta-percha and caoutchouc by air may be conveniently studied by examining the resin of pontianac (Dead Borneo, Besk), which can be readily obtained and at little cost. Pontianac consists of about 70 per cent. of resin and 30 of caoutchouc; the resin has been proved to stand in the same relationship to the caoutchouc substance as the resin of gutta-percha to

gutta-percha itself. A compound, $C_{50}H_{80}O_2$, isolated from the mixture of pontianac resins, melts at 161° , and when dissolved in chloroform gives the same reaction with sulphuric acid as spherite alban.

E. W. W.

Colophony. WILHELM FAHRION (*Zeit. angew. Chem.*, 1904, 17, 239—241. Compare Abstr., 1902, i, 165).—The author maintains that his autoxidation theory with respect to colophony is correct.

A. McK.

A Copal Resin and a New Kino yielded by the Fruit and Bark respectively of *Dipteryx Odorata*. EDOUARD HECKEL and FREDERIC SCHLAGDENHAUFEN (*Compt. rend.*, 1904, 138, 430—432).—A new kino or tanno-glucose was obtained during September by oblique incision of the bark of *Dipteryx odorata* in French Guiana. The trees were fifteen years of age and fully grown. The product is reddish-brown in colour, but transparent; it is slightly soluble in water and possesses a bitter taste. Ferric chloride and ammonia produce a violet colour in the aqueous solutions, the latter are also coloured violet by boiling with finely-divided iron; the addition of acids changes the violet to a red coloration. Aqueous solutions of the kino reduce potassium ferrieyanide to the ferrocyanide. When the resin is heated in the dry state, catechol is formed. The ash after ignition forms 0.15 per cent. of the whole; it contains iron, manganese, and calcium.

S. S.

Caricari Elemi. ALEXANDER TSCHIRCH and L. REUTTER (*Arch. Pharm.*, 1904, 242, 117—121. Compare Abstr., 1902, i, 812; 1903, i, 430).—The sample examined was exhibited as "caricari" at the Brazilian Exhibition of 1886 in Berlin; it had an acid number 27 and saponification number 59. From the solution in ether, 1 per cent. aqueous ammonium carbonate extracted isocarielemenic acid, $C_{38}H_{56}O_4$; this melts at $75-76^\circ$, and is monobasic, with the acid number 90. From the mother liquor, one per cent. aqueous sodium carbonate then extracts two acids; from a solution of these in ether-alcohol carielemic acid, $C_{38}H_{56}O_4$, crystallises; this melts at 215° , and is monobasic, with acid number 94. The amorphous carielemic acid, $C_{37}H_{56}O_4$, remains in solution; this melts at 120° and is monobasic, with acid number 87.

The residual solution, after distillation of the ether, yielded a volatile essential oil on distillation with steam; a bitter-substance was also present. The residue was dissolved in ether-alcohol; crystals separated having the composition $C_{30}H_{50}O$ and $D([\alpha]_D^{25}) + 90^\circ 35'$. These, when benzoylated, yielded the benzoates of α -amyrin and β -amyrin. The substance remaining in the ether-alcohol solution was carieleresen, $C_{24}H_{46}O_2$; it melts at $75-76^\circ$.

In 100 parts of the drug were found: isocarielemenic acid, 5; carielemic acid, 12; carielemic acid, 20; essential oil, 3; amyrins, 3; carieleresen, 40; bitter-substance, impurities, loss, &c., 17 parts.

C. F. B.

Mastic. ALEXANDER TSCHIRCH and L. REUTTER (*Arch. Pharm.*, 1904, 242, 104—110).—The sample examined came from Chios; it had acid number 59 and saponification number 82.5. From the ethereal solution, 1 per cent. aqueous ammonium carbonate extracted the isomeric α - and β -masticic acids, $C_{23}H_{36}O_4$, which were separated by means of the respective insolubility and solubility of their lead salts in alcohol; they are amorphous, and monobasic with acid numbers 141 and 132 respectively; they melt at 90 — 91° and 89.5 — 90.5° .

One per cent. aqueous sodium carbonate then extracts a mixture of acids; that portion of the mixture which forms lead salts insoluble in alcohol was dissolved in alcohol, from which *masticolic acid*, also $C_{23}H_{36}O_4$, crystallised out; this melts at 201° , and is monobasic, with acid number 132; its *silver* salt was analysed. In the alcohol, amorphous α -masticonic acid, $C_{32}H_{48}O_4$, remained dissolved; this melts at 96 — 96.5° , and is monobasic, with acid number 107. Isomeric with this is the acid of which the lead salt is soluble in alcohol, β -masticonic acid; it melts at 91 — 92° , and is monobasic, with acid number 104.

From the remaining ethereal solution, aqueous potassium hydroxide extracts nothing. After the ether had been distilled off, the residue was distilled with steam, when an *essential oil* came over, and a resin remained; a *bitter-substance* is also present. Part of the resin, α -masticoresen, $C_{35}H_{56}O_4$, is soluble in alcohol; this part is amorphous and melts at 74 — 75° . The part insoluble in alcohol, β -masticoresen, is gummy in consistency.

In 100 parts of the drug were found: α - and β -masticic acids, 4; masticolic acid, 0.5; masticonic acid: α , 20; β , 18; masticoresens: α , 30; β , 20; essential oil, 2; bitter-substance, impurities, &c., 5.5 parts.

C. F. B.

Theory of Dyeing. ARTHUR BINZ and GEORG SCHROETER (*Ber.*, 1904, 37, 727—730).—A reply to von Georgievics (this vol., i, 81).

W. A. D.

Brazilin and Hæmatoxylin. JOSEF HERZIG and JACQUES POLLAK (*Ber.*, 1904, 37, 631—633. Compare Abstr., 1901, i, 478; 1902, i, 482; Kostanecki and Lloyd, Abstr., 1903, i, 645).—[With GALITZENSTEIN.]—Cold concentrated sulphuric acid converts trimethylbrazilone into an *isomeride*, which forms white crystals, melts at 170 — 173° , and by prolonged boiling with acetic anhydride is converted into β -acetyltrimethyldehydrobrazilin. Alcohol and sulphuric acid convert it into β -trimethyldehydrobrazilin.

[With R. FISCHER.]—Tetramethylhæmatoxyline reacts in quite similar manner, forming a crystalline *isomeride* which melts at 165 — 167° and yields β -acetyltetramethyldehydrohæmatoxylin on acetylation. The constitution of the two new compounds is in process of investigation.

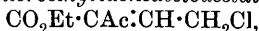
C. H. D.

Nile-blue Base. LEONOR MICHAELIS (*Pflüger's Archiv*, 1904, 101, 183—190).—A reply to Heidenhain (this vol., i, 179). The conclusion

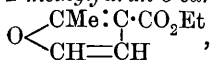
of Heidenhain that proteids behave like acids towards Nile-blue base and that the change in colour, which proteids cause the base to assume, is due to salt-formation, is incorrect. Nile-blue base in dilute alcoholic solution is blue, whilst in concentrated alcoholic solution it is red; the blue coloration is not due to the action of atmospheric carbon dioxide. The reaction between cellulose and Nile-blue base does not necessarily indicate that salt-formation takes place. A. McK.

Synthesis of Furan Derivatives from Chloroacetaldehyde.

GIUSEPPE PLANCHER and S. ALBINI (*Atti R. Accad. Lincei*, 1904, [v], 13, 39—43).—*Ethyl chloroethylideneacetoacetate*,

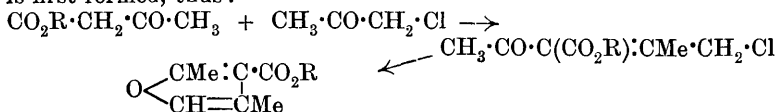


prepared by saturating with hydrogen chloride a cold mixture of ethyl acetoacetate and chloroacetaldehyde hydrate, boils at 105—130° under 19—20 mm. pressure; when heated with alcoholic ammonia at 150° for 4 hours, it gives *ethyl 2-methylfuran-3-carboxylate*,



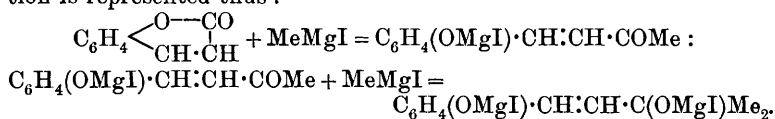
as an oil which, by hydrolysis, is converted into *2-methylfuran-3-carboxylic acid*, crystallising from water and melting at 102—103°.

From these facts, the authors conclude that in the formation of furan or pyrrole derivatives in Hantzsch's synthesis an ethylidene derivative is first formed, thus:

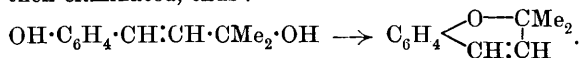


Action of Organo-magnesium Compounds on Lactones. I. JOSEF HOUBEN (*Ber.*, 1904, 37, 489—502).—The author has studied the application of the Grignard reaction to coumarin, the haloids used being methyl iodide, ethyl iodide, *isopropyl* bromide, bromobenzene, benzyl chloride, and α -naphthyl bromide.

2:2-Dimethyl-1:2-chromen, $\text{C}_6\text{H}_4 \begin{array}{c} \text{O} - \text{CMe}_2 \\ \diagdown \quad | \\ \text{CH} : \text{CH} \end{array}$, formed by the action of magnesium methyl iodide on coumarin, is a clear liquid, which boils at 95—96° under 13.5 mm. pressure. It is neutral towards litmus and its solution in concentrated sulphuric acid is purple. Its formation is represented thus:



The latter intermediate compound, when acted on by water, most probably forms dimethyl-*o*-coumaryl alcohol, from which water is then eliminated, thus:



2:2-Diethyl-1:2-chromen, formed in an analogous manner, is a colourless liquid, which boils at 126—127° under 15 mm. pressure. It gives a red coloration with concentrated sulphuric acid and turns brown under the influence of light.

By the action of magnesium isopropyl bromide on coumarin, an oil, boiling at 136—141° under 11 mm. pressure, was obtained; it was probably the diisopropylchromen contaminated with bromine.

The action of magnesium phenyl bromide on coumarin proceeds in a different manner, *diphenyl-o-coumaryl alcohol* (α -diphenyl-o-hydroxycinnamyl alcohol), $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CPh}_2\cdot\text{OH}$, being isolated; it separates from alcohol in crystals melting at 164—166°. It is practically insoluble in an aqueous solution of sodium hydroxide; a phenoxide which is soluble in water with difficulty is, however, actually produced. In virtue of the hydroxyl grouping in the side-chain, it forms carbonium salts (compare Baeyer and Villiger, Abstr., 1902, i, 380, 769). The halochromism of diphenyl-o-coumaryl alcohol is exhibited when its solution in sulphuric acid is shaken with ether; the aqueous acid layer assumes a rosy tint, whilst the ethereal solution is colourless or only faintly yellow. Diphenyl-o-coumaryl alcohol is not converted by concentrated sulphuric acid into diphenylchromen or phenylflavene.

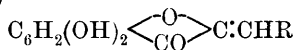
Benzyl o-hydroxystyryl ketone, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$, is formed by interaction of molecular amounts of magnesium benzyl chloride and coumarin, where the latter reacts quantitatively in the enolic form; it is a yellow syrup and boils at 217—219° under 12 mm. pressure. It is soluble with difficulty in a cold aqueous solution of sodium hydroxide.

No definite product was isolated from coumarin and magnesium α -naphthyl bromide. A. McK.

Dihydroxycoumaranone. WLADYSLAW FEUERSTEIN and K. BRASS (*Ber.*, 1904, 37, 817—820).—Dihydroxycoumaranone melts at 229° (compare Nencki, Abstr., 1894, i, 85) and may be formulated as $\text{C}_6\text{H}_4(\text{OH})_2\langle\text{O}\rangle\text{CH}_2$ or $\text{C}_6\text{H}_2(\text{OH})_2\langle\text{C}(\text{OH})\rangle\text{CH}$. The former should yield a diacetyl, and the latter a triacetyl derivative. Analysis is insufficient to determine the number of acetyl groups introduced, and hydrolysis causes complete destruction of the dihydroxycoumaranone. The *acetyl* derivative crystallises from dilute alcohol or light petroleum in slender, almost colourless needles and melts at 106°. Chloroacetyl chloride forms *di-chloroacetoxy coumaranone*, $\text{C}_6\text{H}_2(\text{O}\cdot\text{CO}\cdot\text{CH}_2\text{Cl})_2\langle\text{O}\rangle\text{CH}_2$, crystallising from light petroleum in leaflets and melting at 168°. The composition is determined by an estimation of the chlorine, and proves that dihydroxycoumaranone does not react in the enolic form (compare 5-hydroxycoumaranone, Brühl and Friedländer, Abstr., 1897, i, 221).

Alcoholic hydrogen chloride converts dihydroxycoumaranone into a dark violet condensation product melting above 300°. No hydrazone, oxime, or methyl derivative could be prepared. C. H. D.

Products of Condensation of Dihydroxycoumaranone and Aldehydes. WLADYSŁAW FEUERSTEIN and K. BRASS (*Ber.*, 1904, 37, 821—827. Compare preceding abstract).—Dihydroxycoumaranone condenses with aldehydes to form unsaturated ketones,

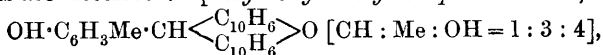


(compare Kesselkaul and Kostanecki, *Abstr.*, 1896, i, 606; Friedländer and Rüdtt, *ibid.*, i, 607; Friedländer and Löwy, *Abstr.*, 1897, i, 32). *p*-Dimethylaminobenzaldehyde forms 1-*p*-dimethylaminobenzylidene-5:6-dihydroxycoumaranone, $\text{C}_{17}\text{H}_{15}\text{O}_4\text{N}$, crystallising from anisole in bluish-violet crystals and melting at 281° . The *diacetyl* derivative, $\text{C}_{21}\text{H}_{19}\text{O}_6\text{N}$, forms violet, glistening needles melting at 215° . 1-*p*-Nitrobenzylidene-5:6-dihydroxycoumaranone, $\text{C}_{15}\text{H}_9\text{O}_6\text{N}$, from *p*-nitrobenzaldehyde, forms golden-bronze needles and melts above 360° ; its *diacetyl* derivative melts at 219° . The *m*-nitro-compound forms yellow needles and melts at 274° , and the *o*-nitro-compound forms slender, yellow needles, and melts at 278° . 1-*m*-Nitro-*p*-dimethylaminobenzylidene-5:6-dihydroxycoumaranone, $\text{C}_{17}\text{H}_{14}\text{O}_6\text{N}_2$, forms slender, red needles and melts above 250° , its *diacetyl* derivative forms yellowish-red crystals and melts at 212° . 1-*o*-Chlorobenzylidene-5:6-dihydroxycoumaranone, $\text{C}_{15}\text{H}_9\text{O}_4\text{Cl}$, crystallises from dilute alcohol in yellow needles or leaflets, the latter having a green lustre, and melts at 253° . 1-*p*-Methylbenzylidene-5:6-dihydroxycoumaranone, $\text{C}_{16}\text{H}_{12}\text{O}_4$, from *p*-tolualdehyde, forms greenish-yellow scales and melts at 276° . 1-*p*-Methoxybenzylidene-5:6-dihydroxycoumaranone, $\text{C}_{16}\text{H}_{12}\text{O}_5$, forms slender, golden-yellow needles and melts at 252° . Concentrated alkali hydroxides decompose it on warming, forming anisaldehyde. 1-Cinnamylidene-5:6-dihydroxycoumaranone, $\text{C}_{17}\text{H}_{12}\text{O}_4$, crystallises in yellow, glistening scales and melts at 236° , dilute sodium hydroxide dissolves it to a deep violet solution, concentrated alkali sets free cinnamaldehyde on warming. 1-*p*-Nitrocinnamylidene-5:6-dihydroxycoumaranone, $\text{C}_{17}\text{H}_{11}\text{O}_6\text{N}$, forms dark red leaflets with bluish-violet reflex and melts at about 265° . 1-*p*-Dimethylaminocinnamylidene-5:6-dihydroxycoumaranone, $\text{C}_{19}\text{H}_{17}\text{O}_6\text{N}$, forms small, dark violet crystals and melts at 262° ; its ethereal solution is fluorescent. The *diacetyl* derivative forms small, dark red needles and melts at 206° .

All the compounds described possess marked dyeing properties, and their behaviour towards various mordants is recorded in the paper.

C. H. D.

New Dinaphthapyranic [Dinaphthaxanthyl] Phenols ROBERT FOSSE (*Compt. rend.*, 1904, 138, 282—284).—The author has previously shown (compare this vol., i, 83) that the dinaphthaxanthonium salts condense with the sodium salts of phenol, β -naphthol, or guaiacol to form derivatives in which the dinaphthaxanthyl residue takes the para-position to the hydroxyl group of the phenol when possible or, failing that, the ortho-position. In the present paper, the condensation products of dinaphthaxanthonium salts with *o*-, *m*-, and *p*-cresols are described. *p*-Hydroxy-*m*-tolylidinaphthaxanthyl,



the *o*-cresol derivative, is a pale red, crystalline solid melting at 232—233°, insoluble in aqueous, but soluble in alcoholic alkali solutions; it forms an acetyl derivative, which melts at 240° and is hydrolysed on boiling with alcoholic alkali solutions. *p*-Hydroxy-*o*-tolylidinaphthaxanthen [CH : Me : OH = 1 : 2 : 4], the *m*-cresol derivative, melts at 215°, and is soluble in benzene and alcoholic alkali solutions, but insoluble in aqueous alkali solutions; it forms colourless, crystalline, molecular combinations with 1 molecular proportion of ethyl alcohol, acetone, or acetic acid, which are not dissociated at 110°. *o*-Hydroxy-*m*-tolylidinaphthaxanthen [CH : Me : OH = 1 : 3 : 6], the *p*-cresol derivative, melts at 249—250°, is soluble in alcoholic, but insoluble in aqueous alkali solutions; its acetyl derivative melts at 232—233°, and its ethyl ether melts at 240—241°, and is insoluble in cold alcoholic or aqueous alkali solutions. M. A. W.

Union of Dinaphthaxanthonium Salts with Tertiary Aromatic Amines. ROBERT FOSSE (*Compt. rend.*, 1904, 138, 575—577).—When dinaphthaxanthonium bromide is mixed with dimethylaniline, the hydrobromide of dimethyl-*p*-aminophenyldinaphthaxanthen is formed.

The base, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \left\langle \begin{smallmatrix} \text{C}_{10}\text{H}_6 \\ \text{C}_{10}\text{H}_6 \end{smallmatrix} \right\rangle \text{O}$, is a white, crystalline solid, which melts at 207—208°, and is soluble in benzene, chloroform, or acetic acid. Diethyl-*p*-aminophenyldinaphthaxanthen, obtained in similar manner, melts at 230—231°. A proof of the constitution of these substances is afforded by the fact that they are also produced from the corresponding aminoaldehyde and β -naphthol; for example, the dimethyl derivative is formed by the action of dimethyl-*p*-aminobenzaldehyde (1 molecule) on β -naphthol (2 molecules) in presence of acetic anhydride and strong sulphuric acid. S. S.

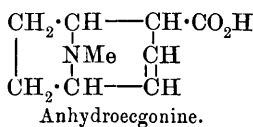
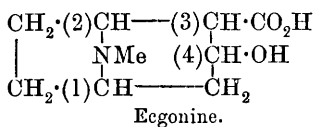
Liebermann's Thiophen Reaction. CARL SCHWALBE (*Ber.*, 1904, 37, 324—325).—Several samples of commercial "pure" benzene which were known to contain thiophen failed to respond to Liebermann's test, giving only a dirty brown, instead of the ordinary dark blue, coloration. Formerly all samples of benzene prepared from the coal tar of gas works responded to the test, but it is probable that the modern German method of obtaining benzene as one of the products of coke manufacture gives rise to a new impurity in the benzene which masks the reaction. W. A. D.

Optical Function of the Asymmetric Carbon Atoms in Ecgonine. JOHANNES GADAMER and T. AMENOMIYA (*Arch. Pharm.*, 1904, 242, 1—16).—Einhorn and Marquardt's conclusion that the anhydroecgonine obtained from *d*- ψ -ecgonine is identical with that from *l*-ecgonine (Abstr., 1890, 646) is confirmed by a comparison of the optical activity of the two products. Moreover, when anhydroecgonine is heated on the water-bath with 33 per cent. aqueous potassium hydroxide, a treatment which converts *l*-ecgonine into *d*- ψ -ecgonine, its optical rotation is unchanged; evidently that asymmetric carbon system which in *l*-ecgonine undergoes inversion can no longer be present in anhydroecgonine.

Hydroecgonine was prepared by reducing anhydroecgonine with sodium in boiling amyl-alcoholic solution (Willstätter, Abstr., 1897, i, 384). The aurichloride was not obtained with $3\text{H}_2\text{O}$, but with $5\text{H}_2\text{O}$, melting at 227° , and also anhydrous, melting at 233° . The hydrochloride was found not to be inactive, but to have a slight lævorotation; this is shown not to be due to an admixture of anhydroecgonine, but it might be caused by a little *l*-ecgonine hydrochloride. When anhydroecgonine is boiled with amyl-alcoholic sodium amyloxide, its rotation is not changed; probably, therefore, its three asymmetric carbon systems persist unchanged in hydroecgonine.

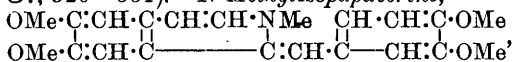
Anhydroecgonine dibromide hydrobromide (Eichengrün and Einhorn, Abstr., 1891, 66) has $[\alpha]_D + 30^\circ$ in 3 per cent. solution. When an attempt was made to obtain a better yield by using only a gentle heat, a salt was obtained which melted at the same temperature, and also yielded a perbromide (dibromo-compound) melting at 145° ; it crystallised with $4\text{H}_2\text{O}$, however, instead of $3\text{H}_2\text{O}$, and was lævorotatory with $[\alpha]_D - 82^\circ$ in 3 per cent. solution. Attempts to convert into hydroecgonine by the action of zinc and acetic acid or of zinc-palladium and concentrated hydrochloric acid were unsuccessful, anhydroecgonine being regenerated. Hydrobromoanhydroecgonine hydrobromide (*loc. cit.*, 94) has $[\alpha]_D + 42^\circ$ in 1 per cent. solution.

By a consideration of these results and those of other investigators, the conclusion is reached that anhydroecgonine has the formula appended, and that in *l*-ecgonine the asymmetric systems 1, 2, 3, 4 are respectively *l*, *d*, *l*, *l*, whilst in *d*- ψ -ecgonine 4 is *d*; the system 4 must cause a rotation of $\pm 39^\circ$ (compare Abstr., 1902 i, 174).



C. F. B.

Papaverinium Bases. HERMAN DECKER and OSKAR KLAUSER (*Ber.*, 1904, 37, 520—531).—*N*-Methylisopapaverine,



prepared by the action of sodium hydroxide on papaverine methiodide, forms transparent, yellow, hygroscopic, monoclinic crystals $[a : b : c = 0.8841 : 1 : 0.8188; \beta = 96^\circ 15']$, and melts at 129 — 131° . Its aqueous solution reacts alkaline towards litmus, and reduces copper sulphate solution. The solution contains the quaternary papaverine hydroxide, from which the yellow base may be regenerated either by concentration of the aqueous solution or by the addition of sodium hydroxide. The *picrate* melts at 129 — 130° .

N-Ethylisopapaverine melts at about 101° ; its *picrate* melts at 154 — 155° . In aqueous solution of the base, the transformation into ethylpapaverinium hydroxide takes place.

N-Benzylisopapaverine, prepared by the addition of sodium hydroxide solution to a solution of papaverine benzyl chloride, separates

from alcohol in golden-yellow scales and melts at 139—140°. In contradistinction to the bases just described, the equilibrium with the corresponding hydroxide is very slowly attained in aqueous solution. Its *picrate* melts at 192°.

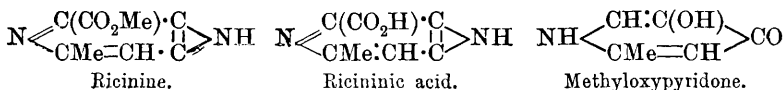
When a current of air was passed through a 1 per cent. solution of *N*-benzylisopapaverine to which sufficient sodium hydroxide solution had been added to cause a faint turbidity, an intense odour of methylvanillin was soon developed; the oxidation was complete after several days. The crystalline product which separated proved to be 6:7-dimethoxy-2-benzyl-1-isoquinolone, $C_9NH_4O(OMe)_2 \cdot C_6H_5$, which crystallises from alcohol in silky needles and melts at 167°. Its *picrate* melts at 133°.

Veratric acid was also obtained in small amount as a product of the oxidation of *N*-benzylisopapaverine; its presence is due to the oxidation of the methylvanillin initially formed.

6:7-Dihydroxy-2-benzyl-1-isoquinolone, prepared by the removal of the methoxyl groups from the preceding dimethoxyquinolone, separates from xylene in lustrous, silvery scales and melts at 225°.

A. McK.

Ricinine. LÉON MAQUENNE and LOUIS PHILIPPE (*Compt. rend.* 1904, 138, 506—508. Compare Tuson, *Trans.*, 1864, 17, 195; Schulze, *Abstr.*, 1898, i, 42; Evans, *Abstr.*, 1900, i, 309).—The ricinine used in this investigation was obtained from the commercial cakes of ricin, and the yield amounted to about 0.2 per cent. Pure ricinine, $C_8H_8O_2N_2$, melts at 201.5° (corr.), and loses one mol. of methyl alcohol on saponification with potassium hydroxide, yielding ricinic acid, $C_7H_6O_2N_2$, which crystallises in slender, brilliant needles, decomposes at 320°, is almost insoluble in cold, but soluble in 100 parts of boiling water. Ricinic acid is readily decomposed by heating to 150° in a sealed tube with hydrochloric acid with the elimination of carbon dioxide and ammonia, and the formation of the hydrochloride of a hydroxymethylpyridone, $C_6H_7O_2N \cdot HCl \cdot 2H_2O$, which melts at 65—70°, becomes anhydrous at 110°, and melts at 155—160°. Hydroxymethylpyridone, $C_6H_7O_2N$, separated from the latter salt by the action of silver oxide or ammonia, crystallises in colourless needles containing one molecular proportion of water of crystallisation, the hydrated compound melts at 80°; the anhydrous, which melts at 170—171°, is readily soluble in warm water or alcohol, and almost insoluble in ice-water; the molecular weight, as determined by the ebullioscopic method in alcohol, confirms the foregoing formula. Ricinine is therefore the methyl ester of an iminomethylpyridine-carboxylic acid, the following formulæ representing the probable constitution of the compound and its two degradation products:



M. A. W.

Preparation of 8-Mono-, Di- and Tri-chloromethylxanthines. C. F. BOEHRINGER & SÖHNE (D.R.-P. 146714. Compare Abstr., 1902, i, 125, 504).—The homologues of xanthine described in the former patents and containing an 8-methyl group may be chlorinated by means of gaseous chlorine acting on a solution or suspension of the compound, or by sulphuryl chloride, phosphorus pentachloride, &c. One, two, or three hydrogen atoms of the methyl group may thus be replaced, yielding stable compounds which have no basic properties. 8-*Chloromethylcaffeine*, $C_9H_{11}O_2N_4Cl$, from 8-methylcaffeine, crystallises from alcohol or ethyl acetate in thick, white needles, melts at 208—210°, and dissolves readily in hot chloroform. 8-*Dichloromethylcaffeine*, $C_9H_{10}O_2N_4Cl_2$, crystallises from alcohol in colourless needles and melts at 230—232°. 8-*Trichloromethylcaffeine*, $C_9H_9O_2N_4Cl_3$, forms white needles melting at 182—184°. 8-*Trichloromethyltheobromine* (3 : 7-dimethyl-8-trichloromethylxanthine), from 8-methyltheobromine, crystallises from ethyl acetate in glistening prisms containing ethyl acetate, which they lose on exposure to air and then melt at 211—212°. C. H. D.

[8-*Trichloromethyl-7-chloromethyl-1 : 3-dimethylxanthine*.] C. F. BOEHRINGER & SÖHNE (D.R.-P. 146715. Compare preceding abstract).—By energetic chlorination of the homologues of 8-methylxanthine, as by the action of gaseous chlorine on a solution in nitrobenzene on the water-bath, the three hydrogen atoms of the 8-methyl group and also one hydrogen atom of the 7-methyl group may be replaced by chlorine. Thus, 8-methylcaffeine yields 8-*trichloromethyl-7-chloromethyl-1 : 3-dimethylxanthine*,

$$\begin{array}{c} \text{NMe} \cdot \text{CO} \cdot \text{C} \cdot \text{N}(\text{CH}_2\text{Cl}) \\ \text{CO} \cdot \text{NMe} \cdot \text{C} \text{---} \text{N} \geq \text{C} \cdot \text{CCl}_3 \end{array}$$
crystallising from alcohol in large, colourless prisms and melting at 204—205°. C. H. D.

2-Methylpyrroline and 1:2-Dimethylpyrroline. LUIGI MAS-CARELLI and GIUSEPPE TESTONI (*Gazzetta*, 1903, 33, ii, 312—318).—The abnormal properties of Hielscher's 2-methylpyrroline and 1:2-dimethylpyrroline (Abstr., 1898, i, 338) is probably due to their containing the double linking between positions 2 and 3; their structures would then be $\text{NH} \begin{array}{l} \text{CMe} \cdot \text{CH} \\ \text{CH}_2 \text{---} \text{CH}_2 \end{array}$ and $\text{NMe} \begin{array}{l} \text{CMe} \cdot \text{CH} \\ \text{CH}_2 \text{---} \text{CH}_2 \end{array}$. They differ from the ordinary methylpyrrolines in being less stable in the air or on distillation, but are somewhat more resistant than these to potassium permanganate, although their stability in this respect is not sufficient to justify the assumption of a double linking between carbon and nitrogen. Attempts, however, to prove the existence of the :NH radicle in the 1-methylpyrroline by means of nitrous acid and by phenylcarbimide failed, but this is explained by the presence of the adjacent methyl radicle. By reduction with tin and hydrochloric acid, the 1-methylpyrroline is converted into 1-methylpyrrolidine; with methyl iodide, it forms a *methiodide*, $\text{MeI} \cdot \text{NH} \begin{array}{l} \text{CMe} \cdot \text{CH} \\ \text{CH}_2 \text{---} \text{CH}_2 \end{array}$, which crystallises from absolute alcohol in large, rectangular plates, melts

and decomposes at 260° , and is converted by aqueous potassium hydroxide into Hielscher's 1:2-dimethylpyrroline.

On bromination in glacial acetic acid, the 1:2-dimethylpyrroline gives a *dibromo-1:2-dimethylpyrroline hydrobromide*, which crystallises from absolute alcohol in orange-yellow, striated leaflets melting at 125° .

W. A. D.

Compounds of Metallic Thiocyanates with Organic Bases. HERMANN GROSSMANN (*Ber.*, 1904, 37, 559—569).—*Pyridine silver thiocyanate*, $\text{AgSCN} \cdot \text{C}_5\text{H}_5\text{N}$, separates from solution in pyridine in decimetre-long (?), glistening, prismatic needles, which soon lose their lustre by exposure to air, liberate pyridine slowly at atmospheric temperatures, but completely at 110° .

Pyridine cuprous thiocyanate, $\text{CuSCN} \cdot 2\text{C}_5\text{H}_5\text{N}$, separates from pyridine in yellow, thin prisms, or stouter crystals of darker colour, and dissociates in the air.

Pyridine lead thiocyanate, $\text{Pb(SCN)}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$, crystallises from pyridine in well-formed, glistening, orthorhombic prisms of pale yellow colour, is more stable in the air than the silver and cuprous compounds, and is decomposed by water, yielding pyridine and a basic salt.

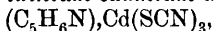
Manganese thiocyanate, $\text{Mn(SCN)}_2 \cdot 3\text{H}_2\text{O}$, prepared by the action of manganese sulphate on barium thiocyanate, separates from the green, syrupy aqueous solution in large, green crystals which soon effloresce in the air. An excess of pyridine precipitates from an aqueous solution of the salt a *compound*, $\text{Mn(SCN)}_2 \cdot 4\text{C}_5\text{H}_5\text{N}$, which crystallises from aqueous pyridine, alcohol, or anhydrous pyridine in glistening, colourless, monoclinic prisms, which show strong interference colours, but are not stable in the air. Manganous thiocyanate forms the *compound* $\text{Mn(SCN)}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$, which separates from an alcoholic solution in yellow, crystalline masses.

A *hexapyridine manganous bromide*, $\text{MnBr}_2 \cdot 6\text{C}_5\text{H}_5\text{N}$, was prepared by crystallising manganous bromide from anhydrous pyridine; it separates in four-sided, glistening, pale-green, rhombohedral tablets and soon effloresces in the air.

Anhydrous nickel thiocyanate, Ni(SCN)_2 , forms a dark chocolate-coloured, amorphous powder which, when covered with water, becomes yellow and finally yields a green solution.

The *compound*, $\text{Ni(SCN)}_2 \cdot 4\text{C}_5\text{H}_5\text{N}$, is precipitated by an excess of pyridine from an aqueous solution of the thiocyanate as a blue, crystalline precipitate, and crystallises from water, alcohol, or pyridine in beautiful, glistening, clear-blue, monoclinic, prismatic needles.

Tetrapyridine cadmium thiocyanate, $\text{Cd(SCN)}_2 \cdot 4\text{C}_5\text{H}_5\text{N}$, prepared by crystallising cadmium thiocyanate from pyridine, separates in long, glistening, colourless, monoclinic prisms, which lose pyridine on exposure to air. *Dipyridine cadmium thiocyanate*, $\text{Cd(SCN)}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$, prepared by the action of pyridine on a cold aqueous solution of cadmium thiocyanate, is precipitated in the form of heavy, white, microscopic needles. *Pyridinium cadmium thiocyanate*,



prepared by dissolving cadmium thiocyanate in aqueous pyridine thio-

cyanate at 100° , forms colourless prisms. *Pyridinium cadmium chloride*, $(C_5H_5N)CdCl_2$, prepared by dissolving dipyridine cadmium chloride in aqueous hydrogen chloride, separates, on concentrating the solution, in long, colourless, monoclinic needles. *Pyridinium cadmium bromide*, $(C_5H_5N)CdBr_2$, prepared by a similar method, crystallises in hexagonal tablets.

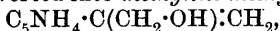
Tetrapyridine zinc thiocyanate, $Zn(SCN)_2 \cdot 4C_5H_5N$, prepared by crystallising zinc thiocyanate from pyridine, forms glistening, prismatic, monoclinic crystals. *Dipyridine zinc thiocyanate*, crystallises from alcohol in thin, prismatic, colourless, monoclinic needles. Water decomposes the zinc and cadmium compounds.

Pyridinium zinc bromide, $(C_5H_5N)_2ZnBr_2$, prepared by dissolving pyridine zinc bromide, $ZnBr_2 \cdot 2C_5H_5N$, in hydrobromic acid, crystallises readily in soluble, colourless, stout, monoclinic prisms. *Pyridinium zinc thiocyanate*, $(C_5H_5N)Zn(SCN)_4$, separates in thin, monoclinic prisms. T. M. L.

Gold Salts of Pyridine Bases. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1903, 1082—1083).—The author points out that he has already described (Abstr., 1881, 56 and 288) gold salts of β -lutidine analogous to those of pyridine described by François (Abstr., 1903, i, 652). T. A. H.

Action of Formaldehyde on α -Picoline (2-Methylpyridine). ANDREAS LIPP and J. RICHARD (*Ber.*, 1904, 37, 737—746. Compare Koenigs and Happe, Abstr., 1903, i, 850).—*Dimethylol-2-picoline* [*2- α -dihydroxyisopropylpyridine*], $C_5NH_4 \cdot CH(CH_2 \cdot OH)_2$, is prepared with a good yield by heating 2-picoline with 40 per cent. formaldehyde for 20 hours at 130 — 140° ; hydroxymethyl-2-picoline (2-picolyalkine) is probably first formed, as, when heated with formaldehyde under the given conditions, it is converted into the dimethyl derivative. When purified by means of its mercurichloride, it crystallises from absolute alcohol on adding anhydrous ether in colourless prisms or needles and melts at 78° . The *mercurichloride*, $C_8H_{11}O_2N \cdot HCl \cdot 6HgCl_2$, forms white nodules and crystals and melts at 161 — 162° ; the *platinichloride* melts at 138 — 139° and decomposes at 142° ; the *aurichloride* melts at 123 — 124° ; the picrate melts at 106.5 — 107.5° (Koenigs and Happe give 108 — 110°). The *dibenzoyl* derivative, $C_5NH_4 \cdot CH(CH_2 \cdot OBz)_2$, crystallises from ether in colourless plates or prisms and melts at 90 — 91° ; its *platinichloride* melts at 112 — 114° . The *monoacetyl* derivative, $C_5NH_4 \cdot CH(CH_2 \cdot OH) \cdot CH_2 \cdot OAc$, prepared by acetylation with acetyl chloride at the ordinary temperature, is a colourless oil which gives a crystalline *platinichloride*, $(C_{10}H_{13}O_3N)_2 \cdot H_2PtCl_6 \cdot H_2O$, melting at 155 — 157° . *Dimethylol-2-picoline methochloride*, although not obtained crystalline, gives well-characterised salts; the *mercurichloride*, $C_9H_{14}O_2NCl \cdot 6HgCl_2$, melts at 152 — 154° , the *platinichloride*, $(C_9H_{14}O_2N)_2PtCl_6 \cdot 2H_2O$, after losing its water of crystallisation, melts at 142 — 145° , and the *aurichloride* at 97 — 98° . On oxidising dimethylol-2-picoline with aqueous potassium permanganate, picolinic acid is obtained, showing that both of the methylol groups are in the side-chain.

When dimethylol-2-picoline is distilled under reduced pressure, it loses water and is converted into *methylene-methylol-2-picoline*,



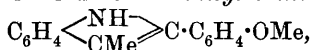
which boils at 135—140° under 10—12 mm. pressure and does not solidify at -20°. The following salts are crystalline; the *hydrochloride* melts at 131—132°, the *mercurichloride*,



at 176—177°, the *platinichloride* decomposes at 170°, and the *aurichloride* and *picrate* melt at 131° and 110—111° respectively. The *acetyl* derivative, $\text{C}_5\text{H}_4\text{N}\cdot\text{C}(\text{CH}_2\cdot\text{OAc})\cdot\text{CH}_2$, is obtained on heating dimethylol-2-picoline with acetic anhydride, and boils at 140—144° under 13 mm. pressure; the *platinichloride* melts at 159—161°. The *dibromide*, $\text{C}_5\text{NH}_4\cdot\text{CBr}(\text{CH}_2\text{Br})\cdot\text{CH}_2\cdot\text{OAc}$, of the acetyl derivative, prepared by adding bromine to its chloroform solution, crystallises from a mixture of alcohol and ether in lustrous prisms and melts at 89—90°. The *benzoyl* derivative, $\text{C}_5\text{NH}_4\cdot\text{C}(\text{CH}_2\cdot\text{OBz})\cdot\text{CH}_2$, crystallises in tufts of prisms, melts at 60—61°, and is easily hydrolysed by boiling hydrochloric acid.

W. A. D.

Indole Derivatives from Anethole. CARL HELL and H. COHEN (*Ber.*, 1904, 37, 866—872. Compare Möhlau, *Abstr.*, 1883, 342; Fischer and Schmidt, *ibid.*, 1888, 698, 958; Bischler, *ibid.*, 1892, 1465; Collett, *Bull. Soc. chim.*, 1897, [iii], 17, 66; Japp and Murray, *Trans.*, 1894, 889; Hell and Günthert, *Abstr.*, 1896, i, 20).—Anisyl bromomethyl ketone, obtained by Hell and Hollenberg's method (*Abstr.*, 1896, i, 354), reacts with aniline in boiling alcoholic solution yielding small amounts of 2-anisyl-3-methylindole,



in the form of glistening plates melting at 123°. A better yield is obtained by working at 120°. 2-Anisyl-3:7-dimethylindole crystallises in colourless needles melting at 127°. 1-Anisyl-3:5-dimethylindole crystallises in glistening plates melting at 134°. α -Naphthylamine and anisyl bromoethyl ketone yield a product melting at 210°.

These indole derivatives do not yield acetyl derivatives (compare Bischler and Fireman, *Abstr.*, 1893, i, 519), and on oxidation give anisic acid and a second acid melting at about 228°. J. J. S.

Indole Derivatives from Ethylisoeugenol. CARL HELL and HERMANN BAUER (*Ber.*, 1904, 37, 872—874).—Aniline and ethylisoeugenole bromoethyl ketone (Hell and Portmann *Abstr.*, 1896, i, 357) in alcoholic solution at 125° yield 2-isoeugenyl-3-methylindole, $\text{C}_6\text{H}_4\left\langle\begin{array}{c}\text{NH} \\ \text{CMe}\end{array}\right\rangle\text{C}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{OEt}$, in the form of colourless plates melting at 165°. It yields an oily *nitrosoamine*, and a red, crystalline *picrate*. On oxidation, ethyl vanillic acid melting at 189° is obtained. *p*-Toluidine and the same ketone yield 2-isoeugenol-3:5-dimethylindole melting at 174°. J. J. S.

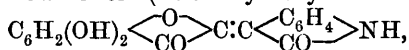
Ammonium Compounds. XV. Synthesis of a Hydroxy-dihydro-base. HANS BÜNZLY and HERMAN DECKER (*Ber.*, 1904, 37, 575—577).—10-Methylacridone, $C_6H_4 \begin{smallmatrix} \text{CO} \\ \text{NM}_6 \end{smallmatrix} C_6H_4$, reacts with magnesium phenyl bromide in the normal manner, and the product mixed with water yields hydroxyphenylmethyldihydroacridine, or, when acidified and treated with sodium bromide solution, yields phenylacridine methobromide (*Abstr.*, 1903, i, 830). The *picrate* melts at 173° .

Acridine methiodide, $C_{14}H_{12}NI$, forms dark red needles and gradually loses methyl iodide.

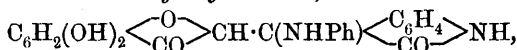
10-Methylacridinium *picrate* melts at 191 — 192° .

J. J. S.

Gallorubin. WLADYSŁAW FEUERSTEIN and K. BRASS (*Ber.*, 1904, 37, 827—831).—Gallorubin (5 : 6-dihydroxyindirubin),



prepared by boiling dihydroxycoumaranone and isatin with hydrochloric acid, crystallises from alcohol in large, brownish-red, prismatic needles, containing 1 mol. alcohol. The compound melts at about 300° . after drying (compare Friedländer and Rüdte, *Abstr.*, 1896, i, 607). Acetic anhydride and sulphuric acid convert it into *triacetyl-gallorubin*, $C_{22}H_{15}O_8N$, crystallising from a mixture of alcohol and chloroform in soft, orange needles and melting at 234° . Gallorubin combines with aniline to form *anilinodihydrogallorubin*,



crystallising from dilute alcohol in small, greenish-yellow leaflets, melting at 257° , and dissolving in alkali hydroxides to a greenish-yellow solution.

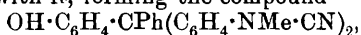
C. H. D.

Basic Diphenylmethane and Triphenylmethane Dyes. JULIUS VON BRAUN (*Ber.*, 1904, 37, 633—646).—The question of the quinonoid structure of di- and tri-phenylmethane dyes may be tested by the preparation of derivatives such that the nitrogen of the amino-groups loses its power of becoming quinquevalent. This is effected by dialkylation and conversion into alkyl-cyano-compounds by the action of cyanogen bromide.

[With E. RÖVER.]—By the gradual addition of cyanogen bromide to partially fused tetramethyldiaminotriphenylmethane, *dicyanodimethyldiaminotriphenylmethane*, $CHPh(C_6H_4 \cdot NMe \cdot CN)_2$, is produced, and separates from alcohol as a white, glistening powder, which melts at 163° , dissolves readily in benzene or chloroform, but is insoluble in water or acids. Concentrated sulphuric acid produces a slight yellow coloration, which is less the purer the cyanide is. Hydrogen sulphide forms the corresponding *thiocarbamide*, $CHPh(C_6H_4 \cdot NMe \cdot CS \cdot NH_2)_2$, which melts at 200° and is insoluble in organic solvents. Boiling hydrochloric acid hydrolyses the cyanide, forming *dimethyldiaminotriphenylmethane*, $CHPh(C_6H_4 \cdot NHMe)_2$, an uncrystallisable base, which may be distilled in steam and melts at 104° ; the *picrate* forms

green needles and melts at 150° . Sodium nitrite forms the *nitrosoamine*, a dark yellow, crystalline powder, melting and decomposing at 149° . Phenylthiocarbimide yields the *phenylthiocarbamide*, $\text{CPh}(\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{CS}\cdot\text{NHPh})_2$, which forms white crystals melting at 124° .

Potassium permanganate in acetone solution oxidises the cyanide to *dicyanodimethyldiaminotriphenylcarbinol*, $\text{OH}\cdot\text{CPh}(\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{CN})_2$, separating from alcohol or acetone as a white, crystalline powder and melting at 168° . It is insoluble in dilute acids, but dissolves in concentrated acids to intensely coloured solutions, from which it is precipitated unaltered by water. Salts with acids could not be isolated. Phenol condenses with it, forming the compound



which melts at 205° . No ether could be obtained by the action of alcohol on the carbinol. On boiling, acids hydrolyse it to *dimethyldiaminotriphenylcarbinol*, $\text{OH}\cdot\text{CPh}(\text{C}_6\text{H}_4\cdot\text{NHMe})_2$, melting at about 95° , and resembling the cyano-compound in its behaviour towards acids. The *zincchloride*, $(\text{C}_{21}\text{H}_{21}\text{N}_2\text{Cl})_2\cdot\text{ZnCl}_2\cdot\text{H}_2\text{O}$, separates from hot water in dark green crystals and melts at 120° . The *nitrosoamine* melts and decomposes at 159° , the *phenylthiocarbamide* melts at 136° , both compounds behave in respect to acids like the carbinol.

The compounds $\text{OH}\cdot\text{CPh}(\text{C}_6\text{H}_4\cdot\text{NRR}')_2$, in which $\text{R}' = \text{CN}$, NO , or $\text{CS}\cdot\text{NHPh}$, and in which the nitrogen is no longer basic, are thus very weak bases in comparison with the tetra-alkylated carbinols. It is therefore concluded that they are true carbinol salts, in which the acid group is attached to methane carbon, whilst the salts of malachite-green, &c., possess the generally accepted quinonoid constitution, possibly taking up a second group, attached to the carbon atom, in presence of a large excess of concentrated acid, when the colour changes from green to red.

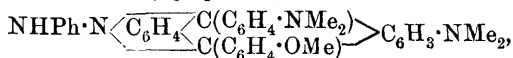
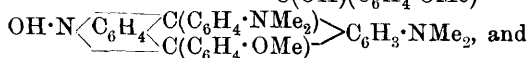
C. H. D.

Electrochemical Reduction of Nitro-compounds of the Naphthalene, Anthracene, and Phenanthrene Series. JOHANNES MÖLLER (*Chem. Centr.*, 1904, i, 461—462; from *Elektrochem. Zeit.*, 10, 199—202, 222—226. Compare *Abstr.*, 1901, i, 598, 646).—The nitro-compounds were dissolved in acid, a mixture of glacial acetic acid and sulphuric acid being usually employed. The current passed from a platinum anode in a porous cell to a cylindrical lead cathode of Tafel's pattern. By the reduction of 1:5- and 1:8-dinitronaphthalenes, 1:5- and 1:8-diaminonaphthalenes were formed respectively, but attempts to prepare nitronaphthylamines and tetrahydrodiaminonaphthalenes failed. 1:5-Dinitroanthraquinone, 2-nitrophenanthraquinone, and 2:7-dinitrophenanthraquinone, when reduced under similar conditions, yielded 1:5-diaminoanthraquinone, 2-aminophenanthraquinone, and 2:7-diaminophenanthraquinone respectively. Since attempts to isolate intermediate products failed in every case, a partial reduction of the nitro-groups cannot occur. The experiments also show that the carbonyl groups are not reduced.

A brief description of other experimental details is also given in the abstract.

E. W. W.

Some Derivatives of Tetramethyldiaminophenyloxanthranol. ALFRED GUYOT and STEHLING (*Compt. rend.*, 1904, 138, 211—213. Compare Haller and Guyot, *Abstr.*, 1901, i, 350; 1903, i, 200, 348; this vol., i, 83).—Tetramethyldiaminophenyloxanthranol condenses readily with anisole to form a white, crystalline product melting at 176°, which is very soluble in benzene, and less so in alcohol or ether; it gives a white, crystalline condensation product with hydroxylamine melting at 203°, soluble in benzene and cold alcohol, and a yellow, crystalline condensation product with phenylhydrazine melting at 213°, soluble in benzene, and less so in alcohol. The formulæ ascribed to these compounds are: $C_6H_4 \begin{smallmatrix} \diagup C(OH)(C_6H_4 \cdot NMe_2) \\ \diagdown C(OH)(C_6H_4 \cdot OMe) \end{smallmatrix} > C_6H_3 \cdot NMe_2$;

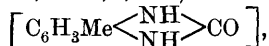


respectively.

The following similar series of compounds were obtained by condensing tetramethyldiaminophenyloxanthranol and phenetole: (1) a crystalline, reddish-brown zincchloride melting at 199°, (2) a white, crystalline base, $C_{32}H_{34}O_3N_2$, melting at 175°, (3) a white, crystalline condensation product with hydroxylamine melting at 208°, (4) a yellow, crystalline condensation product with phenylhydrazine melting at 186°.

M. A. W.

[Preparation of Aromatic Carbamides.] KALLE & Co. (D.R.-P. 146914. Compare *Abstr.*, 1903, i, 555).—*m*-Tolylenecarbamide,



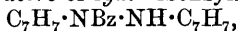
prepared by passing phosgene gas into a solution of *m*-tolylenediamine and sodium acetate so long as a precipitate is formed, is a white, crystalline powder, insoluble in ordinary solvents or in dilute acids or alkalis, and melts above 300°.

m-Phenylenecarbamide is a greyish-white, crystalline powder, insoluble in dilute acids or alkalis; 1:3-naphthylenecarbamide-6-sulphonic acid dissolves in warm water or in alkalis.

C. H. D.

Monobenzoyl Derivatives of the Two Dibenzylhydrazines. G. EBERHARDT and ROBERT BEHREND (*Annalen*, 1903, 329, 363—366).—Behrens and Behrend (*Abstr.*, 1902, i, 752) found, among the products of decomposition of bisnitrosylbenzyl, a substance, $C_{21}H_{20}ON_2$, having the composition of a monobenzoyldibenzylhydrazine, and melting at 168—169°.

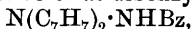
The monobenzoyl derivative of *sym*-dibenzylhydrazine,



could not be prepared by partially hydrolysing the dibenzoyl derivative, but was obtained by suspending the pure hydrochloride in ether or benzene, and adding the calculated quantities of sodium carbonate (calcined) and benzoyl chloride, and then boiling for a short time; the compound crystallises in plates or prisms melting at 85—87°, that is,

at the same temperature as β -benzoyl- β -benzyl- α -benzylidenehydrazine, which Curtius (Abstr., 1902, i, 831) at first thought was a benzoyl derivative of *sym*-dibenzylhydrazine.

The monobenzoyl derivative of *as*-dibenzylhydrazine,



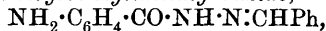
prepared by treating an ethereal solution of the base with dry potassium carbonate and benzoyl chloride, proved to be identical with the substance obtained by Behrens (*loc. cit.*); both specimens crystallise from alcohol in two different forms, one probably belonging to the monoclinic, and the other to the rhombic system; this benzoyldibenzylhydrazine is not changed by prolonged heating with 15 per cent. alcoholic potassium hydroxide or with 33 per cent. sulphuric acid.

K. J. P. O.

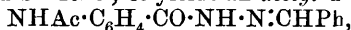
***o*-Aminobenzoylhydrazide and its Derivatives.** C. THODE (*J. pr. Chem.*, 1904, [ii], 69, 92—104).—*o*-Aminobenzoylhydrazide, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$, prepared by the action of hydrazine hydrate on isatoic acid or methyl anthranilate in the presence of alcohol, crystallises in monoclinic prisms from alcohol or short needles from chloroform, melts at 123° , and is easily soluble in hot water and alcohol, but less readily in benzene and ether. The *hydrochloride*, $\text{C}_7\text{H}_9\text{ON}_3 \cdot 2\text{HCl}$, forms an amorphous compound which can be crystallised from alcohol.

At 200° , *o*-aminobenzoylhydrazide loses ammonia, giving *benzoisopyrazolone* [*isoindazolone*], $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NH} \\ \text{CO} \end{smallmatrix} \text{NH}$, which forms prisms, melts at 206° , and, when treated with copper sulphate solution, yields a copper compound, $(\text{C}_7\text{H}_5\text{ON}_2)_2\text{Cu} \cdot \text{CuSO}_4$, in green needles. As *benzoisopyrazolone* is not acted on by acetic anhydride, it is regarded as isomeric with the substance (hydrazinobenzoic anhydride) to which this constitution was assigned by E. Fischer (Abstr., 1880, 647); the structure $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NH} \\ \text{C}(\text{OH}) \end{smallmatrix} \text{N}$ is suggested for the latter.

o-Aminobenzoylhydrazide readily condenses with aldehydes and ketones. *o*-Aminobenzoylbenzylidenehydrazide,

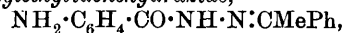


crystallises in colourless needles melting at 195° , very easily soluble in warm alcohol and benzene; it yields an *acetyl* derivative,

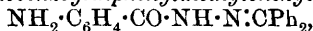


which forms prismatic plates, melts and decomposes at 180° , and is sparingly soluble in alcohol and glacial acetic acid. *Düisopropylidene-aminobenzoylhydrazide*, $\text{CMe}_2 \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{N} : \text{CMe}_2$, or possibly

$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NH} \cdot \text{CMe}_2 \\ \text{CO} - \text{N} \cdot \text{N} : \text{CMe}_2 \end{smallmatrix}$, crystallises in prisms, melts at 244° , is sparingly soluble in acetone, but readily in benzene or alcohol. *o*-Aminobenzoylphenylethyliidenehydrazide,

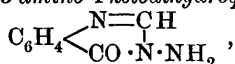


forms prismatic plates, melts at 165° , is fairly readily soluble in benzene and alcohol. *o*-Aminobenzoyldiphenylmethylenehydrazide,



crystallises in needles, melts at 157° , and is readily soluble in acetone, benzene, or alcohol.

On warming with formic acid, *o*-aminobenzoylhydrazide yields a *methenyl* derivative or 3-amino-4-ketodihydroquinazoline,

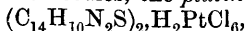


which forms prismatic needles, melts at 204°, and is soluble in alcohol, but less readily so in glacial acetic acid, ether, or water; with benzaldehyde, this yields an anil, $\text{C}_6\text{H}_4 \begin{array}{c} \text{N}=\text{CH} \\ \diagdown \\ \text{CO} \cdot \text{N} \cdot \text{N} \cdot \text{CHPh} \end{array}$, which forms leaflets melting at 129°, soluble in alcohol, less readily so in water and benzene. The corresponding compound, formed with salicylaldehyde, forms aggregates of needles, melts at 205°, and is soluble in alcohol, sparingly so in water, light petroleum, benzene, or ether.

With formic acid, *o*-aminobenzophenylhydrazide similarly yields 3-anilino-4-ketodihydroquinazoline, which forms prisms, melts at 140°, and is soluble in alcohol or benzene, sparingly so in ether or hot water.

Whilst, with *o*-aminobenzoylhydrazide, nitrous acid produces Weddige and Finger's benzoylazoimide, $\text{C}_6\text{H}_4 \begin{array}{c} \text{N}=\text{N} \\ \diagdown \\ \text{CO} \cdot \text{N} \cdot \text{H} \end{array}$ (Abstr., 1887, 667), it gives, with *o*-aminobenzoylphenylhydrazide, the nitroso-derivative, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{NPh} \cdot \text{NO}$, which decomposes at 78° and cannot be crystallised. It is decomposed by hot alcohol, giving slender needles of a compound melting at 206°, and having the composition $\text{C}_{13}\text{H}_{12}\text{ON}_2$.
G. D. L.

Action of Ammonium Persulphate on Thiobenzamide.
REINHOLD VON WALTHER (*J. pr. Chem.*, 1904, [ii], 69, 44—48).—Ammonium persulphate oxidises thiobenzamide energetically to 3:5-diphenyl-1:2:4-thiodiazole, $\text{CPh} \begin{array}{c} \text{S} \cdot \text{N} \\ \diagdown \quad \diagup \\ \text{N} \end{array} \text{CPh}$, which forms white needles melting at 91°, identical with the "dibenzenylazosulphime" obtained by Hofmann and Gabriel (Abstr., 1892, 1109) by the action of iodine on thiobenzamide. The product dissolves in concentrated hydrochloric acid, but the hydrochloride is decomposed by water. The *mercurichloride* forms white needles, the *platinichloride*,

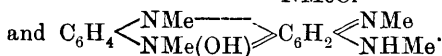
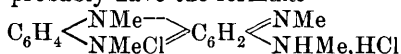


prepared in glacial acetic acid solution, forms microscopic orange needles. Both salts are readily hydrolysed by water. C. H. D.

Preparation of Benziminazoles from Dinitrodiphenylamines.
REINHOLD VON WALTHER and A. KESSLER (*J. pr. Chem.*, 1904, [ii], 69, 40—42).—Alcoholic ammonium sulphide reduces 2:4-dinitrodiphenylamine to 4-nitro-2-aminodiphenylamine, which forms yellow needles melting at 131° and red needles melting at 119°, the latter containing water (compare Nietzki and Almenröder, Abstr., 1896, i, 164). Acetic anhydride converts it into the acetyl derivative, but prolonged boiling with acetic anhydride, or boiling the acetyl derivative with dilute hydrochloric acid, forms 5-nitro-1-phenyl-2-methylbenziminazole, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{array}{c} \text{NPh} \\ \diagdown \quad \diagup \\ \text{N} \end{array} \text{CMe}$, crystallising from alcohol in white

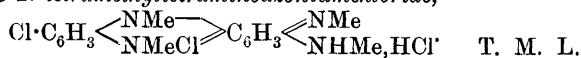
prisms melting at 170° , and forming a characteristic *platinichloride* and *mercurichloride*. Alcoholic ammonium sulphide reduces the base to 5-amino-1-phenyl-2-methylbenziminazole, a brown powder melting at $145-146^{\circ}$.
C. H. D.

Benziminazoles and Oxidation Products of Orthodiamines. OTTO FISCHER (*Ber.*, 1904, 37, 552-558).—When oxidised by means of ferric chloride, dimethyl-*o*-phenylenediamine, $C_6H_4(NHMe)_2$, is converted into the *hydrochloride*, $C_{16}H_{20}N_4Cl_2 \cdot 2H_2O$, of an unstable brownish-yellow azonium base; the hydrochloride separates from alcohol in red flakes with a green lustre and loses hydrogen chloride as well as water when heated at 130° . The *nitrate*, $C_{16}H_{20}O_6N_6$, crystallises from water or dilute alcohol in beautiful, stout prisms with a green, metallic lustre. The *mercurichloride*, $C_{16}H_{19}N_4HgCl_3$, separates from alcohol in needles with a green, metallic lustre. Reduction of the hydrochloride with zinc-dust yields a green solution, whilst tin and hydrochloric acid give methylamine hydrochloride and the tin-salt of a *base*, $C_{15}H_{19}N_3$, which separates from ether in nodular, crystalline masses, gives flashes of light when crushed, melts at 118° , and yields a deep green solution when the hydrochloric acid solution is acted on by ferric chloride, platinic chloride, or dilute nitric acid. The hydrochloride and base probably have the formulæ

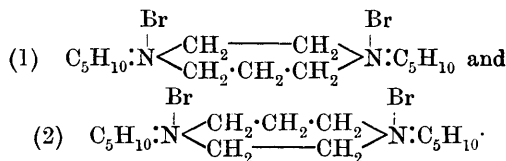


6-Chlorobenziminazole, $C_6H_3Cl \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{CH}$, prepared by the action of formic acid on 4-chloro-*o*-phenylenediamine (m. p. 76° , not 72° as given by Laubenheimer), crystallises from a mixture of benzene and light petroleum in nodular aggregates of colourless needles and melts at 125° ; it separates from hot water in minute, white needles, which melt at 85° when air-dried and at 125° after driving off water of crystallisation. 6-Chloro-1:3-dimethylbenziminazole iodide, $C_9H_{10}N_2ClI$, prepared by heating the preceding compound with methyl alcohol and methyl iodide at $120-130^{\circ}$, crystallises from alcohol in white tablets, and is converted by cold sodium hydroxide into 6-chloro-1:3-dimethylbenziminazolol, $C_8H_3Cl \begin{array}{c} \text{NMe} \\ \diagup \quad \diagdown \\ \text{NMe} \end{array} \text{CH} \cdot \text{OH}$, which crystallises from dilute methyl alcohol in flat, white prisms, melts at 106° , and becomes violet-red on exposure to moist air; its *platinichloride*, $C_{14}H_{12}N_2Cl_6Pt$, separates from hot dilute hydrochloric acid in long, orange-yellow prisms; the aurichloride separates in minute, golden-yellow needles. 4-Chlorodimethyl-*o*-phenylenediamine, $C_6H_3Cl(NHMe)_2$, prepared by boiling chlorodimethylbenziminazolol or the iodide of chlorodimethylbenziminazole with aqueous potassium hydroxide, crystallises from light petroleum in radiating aggregates of prisms, or in long, stout columns, and melts at 61° . Oxidation with ferric chloride yields, as in the previous case, a *hydrochloride*, $C_{16}H_{19}N_4Cl_3 \cdot 2H_2O$, which separates as a paste of crystal flakes with bronze-like lustre, and crystallises from dilute alcohol; the *platinichloride*, $C_{16}H_{19}N_4Cl_7Pt \cdot H_2O$, forms prisms

with a green, metallic lustre; the *iodide* is sparingly soluble and the *nitrate* readily soluble; the *bromide*, $C_{16}H_{19}N_4ClBr_2 \cdot H_2O$, forms beautiful, green needles, somewhat sparingly soluble in water; the *picrate*, $C_{16}H_{17}N_4Cl \cdot 2C_6H_3O_7N_3$, separates from dilute alcohol in dark-coloured needles with a metallic lustre, sparingly soluble in water; the *base* forms unstable, orange-coloured flocks, the hydrochloride is formulated as a *monochloro-N-tetramethyltetraminoazoniumchloride*,



Quinquevalent Nitrogen. I. A New Case of Stereoisomerism. OSSIAN ASCHAN (*Zeit. physikal. Chem.*, 1903, **46**, 293—322. Compare Abstr., 1899, i, 542).—The two substances prepared by the action (1) of trimethylene bromide on dipiperidylethane, (2) of ethylene bromide on trimethylene dipiperidide, are found to be stereoisomeric; they are of the type Na_2bcd , and may be represented as follows:



The concentrated aqueous solution of each of these dibromides is optically inactive. From the first isomeride, ethylenetrimethylenedipiperidylum bromide (m. p. above 300°), a dichloride, a di-iodide (m. p. 300° with decomposition), a platinichloride, and a mercuric chloride double salt ($C_{15}H_{30}N_2Cl_2 \cdot 2HgCl_2$, long, colourless needles, m. p. 189°) have been prepared. From trimethylene-ethylenedipiperidylum bromide, which becomes darker above 300° without showing a definite melting point, a platinichloride, a di-iodide (m. p. 282° , with decomposition), and a mercuric chloride derivative (long, colourless needles, m. p. 192°) have been prepared. The solubility of trimethylene-ethylenedipiperidylum bromide in 75 per cent. alcohol is considerably greater than that of ethylenetrimethylenedipiperidylum bromide, and a similar remark applies to the relative solubility of the two di-iodides in water.

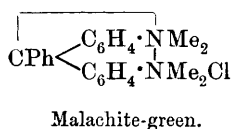
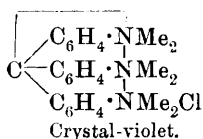
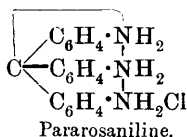
Attempts have been made with the aid of *d*-bromocamphor-sulphonate to resolve these diammonium dibromides into active components, but without success. It appears, therefore, that the bromine atoms must lie in the same plane as the middle ring, and that the two piperidine rings lie in planes perpendicular to that of the middle ring. This is in harmony with van't Hoff's diagram representing the bonds of quinquevalent nitrogen, which, however, may be simplified by supposing the nitrogen atom at the centre of a tetrahedron, four of the bonds going to the corners of the tetrahedron, and the fifth to the centre of gravity of one of the tetrahedron faces.

J. C. P.

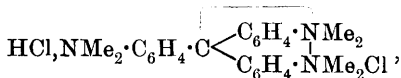
Preparation of Phenylurazole from α -Ethyl Phenylsemicarbazidecarboxylate. SALOMON F. ACREE (*Ber.*, 1904, 37, 618—625. Compare Abstr., 1903, i, 867).—Potassium hydroxide hydrolyses α -ethyl phenylsemicarbazidecarboxylate to *potassium phenylsemicarbazide- α -carboxylate*, $\text{CO}_2\text{K}\cdot\text{NPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, which is converted into *potassium phenylurazole* by heating at 150° . The *silver salt* in similar manner forms silver phenylurazole at 150° . *Potassium phenylthiosemicarbazide- α -carboxylate*, $\text{C}_6\text{H}_5\text{O}_2\text{N}_3\text{SK}\cdot 2\text{H}_2\text{O}$, forms *potassium 1-phenyl-3-thiourazole* at 150° . *Sodium 1-phenyl-4-methylthiosemicarbazide- α -carboxylate* forms *sodium 1-phenyl-4-methyltriazolyl-3-mercaptol* at 130° . The *silver salt* of the mercaptol is crystalline and anhydrous.

C. H. D.

A New Formula for the Basic Triphenylmethane Dyes. GEORG VON GEORGIEVICS (*Zeit. Farb. Text. Chem.*, 1904, 3, 37—39).—In order to explain the progressive diminution in colour of the triaminotriphenyl dyes on adding mineral acids to their solutions, and the fact that to each of the three phenylamino-radicles a definite chromophoric effect is to be attributed (compare Formánek, this vol., ii, 106), the author assumes that the three amino-radicles are intimately connected to form a colour centre, as shown, for example, in the formulæ:



On adding 1HCl to, for instance, crystal-violet, one of the linkings between the nitrogen atoms is broken to form the compound



which, in structure and in the character of its absorption spectrum, resembles dyes of the diaminotriphenylmethane group. With a large excess of hydrochloric acid, the salt, $\text{CCl}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_3\text{HCl}$, is ultimately obtained, which contains no chromophore linkings, and is hence colourless. This theory offers also a simple explanation of the fact observed by Hantzsch, that of the polyacid salts derived from crystal-violet, those of the carbinol base are much less dissociated in aqueous solution than those of the colour base; from the latter, hydrogen chloride is split off in solution because of the tendency of the nitrogen atoms to saturate each other.

W. A. D.

Azo-compounds. Reduction of Nitrobenzoic Acids and Acetals. PAUL FREUNDLER (*Compt. rend.*, 1904, 138, 289—291. Compare Abstr., 1903, i, 371; this vol., i, 121).—When the acetal of

o-nitrobenzaldehyde is reduced by zinc and sodium hydroxide in the presence of alcohol, the chief product is the *acetal* of *o*-azobenzaldehyde, $N_2[C_6H_4 \cdot CH(OMe)_2]_2$ which melts at 144° and gives a hydrazone melting at 115° , the yield is 63 per cent. of the theoretical; there are formed in addition 15 per cent. of a basic aldehyde not yet identified, 5 per cent. of anthranilic acid, and a compound, $C_{14}H_8O_2N_2$, previously obtained in the reduction of *o*-nitrobenzyl-alcohol. The *acetal* of *m*-nitrobenzaldehyde, when similarly reduced, yields 93 per cent. of the theoretical quantity of the *acetal* of *m*-azobenzaldehyde, which melts at 86° , the corresponding aldehyde melting at 150° . The *acetal* of *p*-nitrobenzaldehyde yields on reduction 83 per cent. of the theoretical quantity of the *acetal* of *p*-azobenzaldehyde together with a small quantity of resin analogous to that formed by the reduction of the corresponding aldehyde (compare Alway, Abstr., 1903, i, 201, 425, 706). *o*-Nitrobenzoic acid yields on reduction 62 per cent. of *o*-azobenzoic acid and 10 per cent. of anthranilic acid, whilst under the same conditions, *p*-nitrobenzoic acid yields only *p*-azobenzoic acid.

In the reduction of these two series of compounds, only the ortho-substituted derivatives have given any appreciable quantity of the corresponding amide, and the author suggests that this may be due to steric hindrance.

M. A. W.

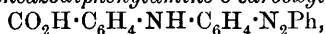
Diazotisation of Nitrobenzene. EUGEN BAMBERGER and ALEXANDER WETTER (*Ber.*, 1904, 37, 629—630).—The rôle of the substances taking part in the process of "diazotisation" may be so far reversed that ammonia (in the form of its sodium derivative) may be made to react with nitrobenzene with the formation of normal sodium diazoxide: $C_6H_5 \cdot NO_2 + NH_2Na = C_6H_5 \cdot N_2 \cdot ONa + H_2O$. The yield is extremely small, but the diazoxide can be recognised by its reaction with phenols. A better result is obtained by mixing sodamide with nitrobenzene and β -naphthol at a low temperature, when a reaction takes place, and benzeneazo- β -naphthol may be isolated from the product. Formation of aniline and sodium nitrite takes place to a small extent, but that this is not the cause of the formation of the diazoxide is shown by the fact that no trace of dye is produced from aniline, sodium nitrite, and β -naphthol in absence of water. When a small quantity of sodamide is warmed with nitrobenzene, sodium *iso*-diazoxide is produced; larger quantities react violently with charring.

C. H. D.

Preparation of Benzeneazodiphenylamines from Aminoazobenzene. REINHOLD VON WALTHER and A. LEHMANN (*J. pr. Chem.*, 1904, [ii], 69, 42—44).—2:4-Dinitrochlorobenzene and aminoazobenzene combine at 130° to form 4'-benzeneazo-2:4-dinitrodiphenylamine, $C_6H_3(NO_2)_2 \cdot NH \cdot C_6H_4 \cdot N:NPh$, separating from glacial acetic acid in orange-red crystals and melting at 175.5 — 176° . Aminoazobenzene and picryl chloride form 4'-benzeneazo-2:4:6-trinitrodiphenylamine, $C_6H_2(NO_2)_3 \cdot NH \cdot C_6H_4 \cdot N:NPh$, crystallising from benzene or acetic acid in golden-yellow leaflets and melting at 176 — 177° .

C. H. D.

Benzeneazodiphenylamine-*o*-carboxylic Acid and its Homologues. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 146950).—*o*-Chlorobenzoic acid reacts with aminoazobenzene in presence of metallic copper or copper salts (compare Abstr., 1903, i, 754), forming *benzeneazodiphenylamine-*o*-carboxylic acid*,



crystallising from alcohol in yellow needles and melting at 221—222°, almost insoluble in hot water, more soluble in hot alcohol. *Toluene-*o*-azo-*o*-tolylphenylamine-*o*-carboxylic acid* crystallises from benzene in needles and melts at 217—218°; *toluene-*p*-azo-*p*-tolylphenylamine-*o*-carboxylic acid* melts at 226—227°.

C. H. D.

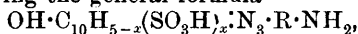
[**Azo-dyes from 4-Chloro-2-aminophenol.**] AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 144618).—Warm concentrated sulphuric acid converts 4-chloro-2-aminophenol into a monosulphonic acid, which may be diazotised and combined with 1:8-aminonaphthol-3:6-(or 2:4)-disulphonic acid, forming dyes which give blue lakes with copper salts.

C. H. D.

Disazo-dye from Chloroaminosalicylic Acid. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 144475).—*p*-Chloro-*o*-aminosalicylic acid, prepared by reduction of the corresponding nitro-acid (Abstr., 1880, 392), forms a *diazonium* compound crystallising in yellow needles, which may be combined with α -naphthylamine-6- or -7-sulphonic acid or a mixture of these. The resulting compound may be again diazotised and combined with β -naphthol. The product is a greenish-black, metallic powder, which dissolves in water to a reddish-violet solution, and forms a soluble, indigo-blue sodium salt.

C. H. D.

Azo-dyes from Aminoaliphylhydroxynaphthyltriazole-sulphonic Acids. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 146375).—Aminoaliphylhydroxynaphthyltriazole-sulphonic acids having the general formula



where R is an aliphyl residue, are prepared by combining nitrophenyl-diazonium salts with naphthylaminesulphonic acids containing an α -sulpho-group, and having an unsubstituted ortho-position relatively to the amino-group. Thus, diazotised *p*-nitroaniline combines with α -naphthylamine-3:6:8-trisulphonic acid, and when the resulting *o*-aminoazo-compound is oxidised by sodium hypochlorite, reduced by iron and acetic acid, and heated with sodium hydroxide, *sodium hydrogen p-aminophenyl-8-hydroxynaphthyl-1:2-triazole-3:6-disulphonate*,

$\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}\begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{C}_{10}\text{H}_3(\text{SO}_3\text{Na})_2\cdot\text{OH}$, is obtained, crystallising in greenish-yellow leaflets. Similar products are obtained from diazotised *m*-nitroaniline or nitrotoluidine and β -naphthylamine-5:7-(or 6:8)-disulphonic acid.

C. H. D.

Preparation of 2:6-Tetrazophenol-4-sulphonic Acid. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 148085).—The tetrazonium compounds of 2:6-diaminoalkyloxybenzene-4-

sulphonic acids readily exchange their alkyloxy-group for hydroxyl, even in acid solution. The course of the reaction may be followed by combining the diazotised compound with β -naphthol. A rapidly prepared solution of the corresponding tetrazonium derivative combines with β -naphthol to form a red azo-compound, whilst a solution which has been prepared for some time yields a characteristic bluish-black disazo-dye. A large excess of acid and a low temperature should be employed during diazotisation, in order to prevent combination of the tetrazonium compound with the unaltered acid. 2:6-Dinitroanisole-4-sulphonic acid, prepared by nitrating anisole-*p*-sulphonic acid, forms a *potassium* salt crystallising in flat, colourless needles, becoming yellow in the light. Reducing agents form the 2:6-diamino-acid, separating in colourless, sparingly soluble needles, from which 2:6-tetrazophenol-4-sulphonic acid may be obtained in the manner described.

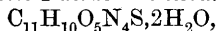
C. H. D.

Diazoamino-compounds of Iminazoles and Purine Derivatives. RICHARD BURIAN (*Ber.*, 1904, 37, 696—707).—Substituted iminazoles of the type $\begin{array}{c} \text{R}^1\text{C}\cdot\text{NH} \\ | \\ \text{R}^2\text{C}-\text{N} \end{array} \gg \text{CR}^3$, which still retain the imino-radicle, interact with diazobenzene salts to form coloured diazoamino-derivatives of the general formula $\begin{array}{c} \text{R}^1\text{C}\cdot\text{N}(\cdot\text{N}:\text{NAr}) \\ | \\ \text{R}^2\text{C}-\text{N} \end{array} \gg \text{CR}^3$.

Iminazole-1-diazobenzenesulphonic acid, $\text{C}_3\text{N}_2\text{H}_3\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, prepared by the action of diazobenzenesulphonic acid or of diazotised sulphanilic acid on an ice-cold dilute alkaline solution of iminazole, crystallises in golden spangles and begins to decompose at $240\text{--}250^\circ$. 2-Methyliminazole-1-diazosulphonic acid, obtained similarly from 2-methyliminazole, is a red, crystalline powder. 2-Phenyl-1-tetrazodiphenyliminazole, $\text{C}_{12}\text{H}_8(\text{N}:\text{N}\cdot\text{C}_6\text{H}_4)_2$, prepared from 2-phenyliminazole (2 mols.) and diazotised benzidine (1 mol.), forms a brownish-red, crystalline powder, which blackens at 260° . 2-Thiol-4:5-diphenyl-1-tetrazodiphenyliminazole, $\text{C}_{12}\text{H}_8(\text{N}:\text{N}\cdot\text{C}_6\text{H}_4)_2\cdot\text{SH}$, obtained in the same way from 2-thiol-4:5-diphenyliminazole (2 mols.) and benzidine forms orange-coloured aggregates of microscopic needles which soften at 110° and melt and decompose at $120\text{--}122^\circ$.

Iminazole-4:5-dicarboxylic acids, when combined with diazobenzenesulphonic acid, evolve carbon dioxide, and are converted into derivatives of iminazolemonocarboxylic acid, but which of the carboxyl radicles is eliminated has not been ascertained. *Carboxyiminazole-1-diazobenzenesulphonic acid*, $(\text{C}_4\text{H}_3\text{O}_2\text{N})\text{N}:\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, prepared from iminazole-4:5-dicarboxylic acid, forms yellow needles or a red, microcrystalline powder and blackens above 265° .

Carboxy-2-methyliminazole-1-diazobenzenesulphonic acid,

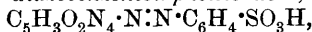


obtained from 2-methyliminazole-4:5-dicarboxylic acid, forms feathery aggregates of needles and darkens at 120° .

Carboxy-2-phenyliminazole-1-diazobenzenesulphonic acid, $\text{C}_{16}\text{H}_{12}\text{O}_5\text{N}_4\text{S}$, forms brownish-red aggregates of microscopic needles.

Purine derivatives, in virtue of the iminazole ring that they contain, are capable of combining with diazo-salts in the same manner; that it is the imino-radicle in position 7 which enters into action is shown by the fact that combination only occurs in the case of those compounds in which the hydrogen atom in position 7 is intact. Theobromine (3:7-dimethylxanthine) and caffeine (1:3:7-trimethylxanthine), for instance, fail to combine with diazobenzenesulphonic acid.

2:6-Dioxy-7-diazobenzenesulphonic acid,



prepared from xanthine and diazobenzenesulphonic acid, crystallises from water in rosettes of yellow needles. 2:6-Dioxy-1:3-dimethyl-purine-7-diazobenzenesulphonic acid, prepared from theophylline, forms lustrous, orange-red needles. The compounds from guanine, hypoxanthine, and adenine form yellowish-red, bright yellow, and brownish-red needles respectively.

It is suggested that the production of colour by the union of a diazo-salt with the purine bases should be used as a qualitative test for these substances. The test is, however, not universally applicable, as its sensitiveness is affected by the presence of impurities, notably of reducing agents.

W. A. D.

The Group of Simplest Proteids (Protamines). ALBRECHT KOSSEL and HENRY D. DAKIN (*Zeit. physiol. Chem.*, 1904, 40, 565—571).—In previous work, aminovaleric acid has been obtained from clupein, tyrosine from cyclopterin, scatoleaminoacetic acid from cyclopterin, pyrrolidine-2-carboxylic acid from salmin, and serin ($\text{C}_3\text{H}_7\text{O}_2\text{N}$) from clupein. The present investigation shows that aminovaleric acid and serin are more widely found; thus salmin yields both in addition to arginine and pyrrolidine-2-carboxylic acid. The protamines of carp sperm are at least two in number (α - and β -cyprinin). On decomposition, they yield basic products, arginine, lysine, tyrosine in small amount, aminovaleric acid, but not histidine. α -Cyprinin does not yield tyrosine.

W. D. H.

The so-called Metallic Derivatives of Proteids from the Point of View of Chemical Equilibrium. GINO GALEOTTI (*Zeit. physiol. Chem.*, 1904, 40, 492—549).—The author has examined a number of precipitates of albumins with metallic salts, more especially those of egg-albumin with copper sulphate and egg-albumin with silver nitrate, from the point of view of the phase rule. The conclusions drawn are: (1) the precipitates, *metal albuminates*, obtained are not true chemical compounds of fixed composition in the sense required by the valency theory, they are indefinite substances varying considerably in composition. (2) The precipitation processes are reversible, and as a rule the precipitate dissolves in excess of one or other of the constituents. (3) The composition of the precipitate depends on the composition of the liquid in contact with it, as required by the thermodynamical laws of chemical equilibrium.

A summary of previous work is also given.

J. J. S.

Physical Changes in the Condition of Colloids. III. Non-reversible Precipitation of Albumin by Electrolytes. WOLFGANG PAULI (*Beitr. chem. Physiol. Path.*, 1903, 5, 27—55. Compare Abstr., 1902, ii, 388; 1903, i, 299).—In contrast to the behaviour of alkali salts, the effect produced on albumin by calcium, strontium, and barium salts is non-reversible. The behaviour of the alkaline earth salts is intermediate between that of the alkali salts and that of heavy metal salts, in which latter case the influence of the cation is the only determining factor. The chlorides and acetates of calcium, strontium, and barium are effective in inducing precipitation of albumin only in much more concentrated solution than the corresponding salts of the alkali metals. On the other hand, precipitation is induced by comparatively dilute solutions of the thiocyanates, iodides, and bromides.

The influence of salts of the alkali metals on the precipitating power of alkaline earth salts has been studied in detail. This power is increasingly intensified by various anions in the order given: $C_2H_3O_2'$, Cl' , NO_3' , Br' , I' , CNS' . Similarly, the alkali cations are arranged in the order: Mg'' , NH_4' , K' , Na' .

A solution of albumin becomes acid on addition of an alkaline earth salt, and it can be shown that in acid solution the changes produced in albumin by alkali salts also are non-reversible. The precipitation by alkaline earth salts, however, takes place equally well in alkaline solution, and the parallelism between the precipitation by alkaline earth salts and by alkali salts in acid solution is due to the firmer attachment of an electropositive ion.

J. C. P.

Artificial Change of Albumin into Globulin. LEOPOLD MOLL (*Beitr. chem. Physiol. Path.*, 1903, 4, 563).—By warming serum to 60° , alkali-albumin is formed and the globulin is increased at the expense of the albumin. By warming to 56° , there is also increase in the globulin, but no formation of alkali-albumin. By similarly warming a dilute alkaline solution of crystalline serum-albumin, it is in part converted into globulin, first pseudo-globulin and then euglobulin. Globulin contains less sulphur than albumin; this is also true for the artificial globulin. Hydroxyl ions are regarded as the cause of the change. Neutral salts, especially of ammonium, inhibit the transformation; sugar acts, to a slight extent, in the same way, but urea hastens it.

W. D. H.

Percaglobulin, a Characteristic Proteid of the Ovary of the Perch. CARL TH. MÖRNER (*Zeit. physiol. Chem.*, 1904, 40, 429—464).—The name *percaglobulin* is given to a proteid which is characteristic of the perch (*Perca fluviatilis*). It is not found in the ova. Like edestin, it readily passes into an insoluble modification (*percaglobulan*). It differs from other known globulins by its astringent taste, its precipitability by dilute hydrochloric acid, its high percentage of sulphur, and the property it has of precipitating certain gluco-proteids and polysaccharides, being itself precipitated at the same time.

W. D. H.

Decomposition Products of Gelatin. PHOEBUS A. LEVENE (*Zeit. physiol. Chem.*, 1904, 41, 8—14, 99—100. Compare Abstr., 1903, i, 301; this vol., ii, 188).—A further account of observations already published.
W. D. H.

Neutral Soluble Silver Compounds of Gelatoses. FARBWERKE VORM MEISTER, LUCIUS, & BRÜNING (D.R.-P. 146792 and 146793).—Solutions of gelatose, prepared by heating gluten with water, may be neutralised by the addition of sodium hydroxide, and converted into the soluble silver derivative by adding insoluble silver compounds, such as silver lactate or silver succinimide, in the state of fine powder. Silver nitrate may also be employed (compare D.R.-P. 141967), the neutralisation being performed after the addition of the silver salt.

C. H. D.

Theoretical Study of the Dissociation of Oxyhæmoglobin. Effects of Concentration and Temperature. VICTOR HENRI (*Compt. rend.*, 1904, 138, 572—574).—Hüfner, when studying the equilibrium of the system: oxyhæmoglobin, hæmoglobin, and oxygen, assumed that one molecule of each of these substances enters into the reactions; the numbers which he obtained for K were not constant, but varied with the concentration of hæmoglobin. It is now shown that Hüfner's experimental data lead to a more constant value for K , if the reaction be represented as oxyhæmoglobin (1 molecule) \rightleftharpoons hæmoglobin (2 molecules) + O_2 . Evidence is also adduced to show that the reaction is highly influenced by variations in temperature.
S. S.

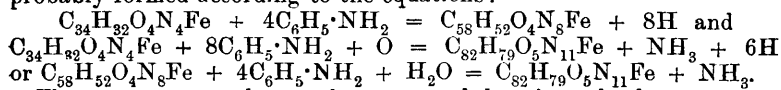
Hæmin from Different Sources, Dehydrochlorohæmin and Hæmatin. WILLIAM KÜSTER (*Zeit. physiol. Chem.*, 1904, 40, 391—422. Compare Abstr., 1902, i, 845).—Nencki and Sieber's hæmin (Abstr., 1885, 69, 825; 1886, 374, 482; 1888, 971), Schalféeff's acetyl hæmin (Abstr., 1885, 566; 1886, 165; Nencki and Zaleski, Abstr., 1900, i, 709; 1901, i, 434), Morner's β -hæmin, and Cloetta's and Rosenfeld's hæmin (Abstr., 1898, i, 542), all have the same composition, $C_{34}H_{33}O_4N_4ClFe$, and the simple name hæmin for all of them is suggested. The substances were all purified and obtained in a crystalline form. On treatment with cold aniline, they lose the elements of hydrogen chloride and yield, after extraction with dilute acetic acid and ether, an amorphous product, *dehydrochlorohæmin*, $C_{34}H_{32}O_4N_4Fe$, which can be converted into hæmin.

Hæmatin, the product obtained by the action of aqueous alkalis on hæmin, has the composition $C_{34}H_{34}O_5N_4Fe$, and appears to be hæmin in which the chlorine has been replaced by hydroxyl; but it cannot be transformed back into hæmin.

Dehydrochlorohæmin, when dissolved in alkali and precipitated by acid, appears to be transformed into an isomeride, *dehydrohæmatin*, since it is no longer capable of being converted into hæmin. Hæmatin hydrobromide (Abstr., 1894, i, 312) has the composition $C_{34}H_{33}O_3N_4BrFe$.

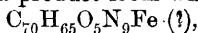
Hæmin, on treatment with alcohol and hydrogen chloride or sulphuric acid, appears to yield ethyl ethers, but nitrogen is removed at the same time. J. J. S.

Action of Boiling Aniline on Hæmin. WILLIAM KÜSTER (*Zeit. physiol. Chem.*, 1904, 40, 423—428).—Boiling aniline reacts with acetyl hæmin yielding two products, $C_{58}H_{52}O_4N_8Fe$ and $C_{82}H_{79}O_5N_{11}Fe$, probably formed according to the equations:



The two compounds may be separated by the aid of acetone, in which the product of lower molecular weight is insoluble.

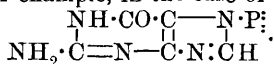
Morner's hæmin gives a product from which a substance,



soluble in acetone, can be isolated.

J. J. S.

State of Combination of the Purine Bases in Nucleic Acid. RICHARD BURIAN (*Ber.*, 1904, 37, 708—712).—Nucleic acid, prepared either from herring's roe, calves' thymus, or yeast, does not form at once a coloured compound with an alkaline solution of diazobenzenesulphonic acid (compare this vol., i, 354). On previously hydrolysing the nucleic acid from yeast, however, with hydrochloric acid, it readily forms a red compound, the analysis of which shows it to be xanthine-diazobenzenesulphonic acid. From the thymonucleic acid, in a similar manner, guaninediazobenzenesulphonic acid is obtained. The author concludes that these observations show that the purine bases of nucleic acid are probably combined with phosphoric acid through the nitrogen atom in position 7; for example, in the case of guanine, thus:



W. A. D.

Hæmase. OSCAR LOEW (*Pflüger's Archiv*, 1903, 100, 332—334. Compare Abstr., 1903, i, 544).—Senter has suggested the name hæmase for the catalase he has found in blood, without any proof that it acts differently from the catalases of plants. The name blood-catalase is suggested to indicate that all such substances decompose hydrogen peroxide in a similar way. W. D. H.

Influence of Hydrogen Ions on Invertase from *Aspergillus Niger*. ARISTIDES KANITZ (*Pflüger's Archiv*, 1903, 100, 547—550).—From Fernbach's results on the influence of the concentration of sulphuric, oxalic, tartaric, succinic, lactic, and acetic acids respectively on invertase from *Aspergillus niger*, the author calculates, by aid of the dissociation constants of the acids referred to, that the invertase reaches its optimum in solutions which are 1/8000 to 1/300*N* with reference to hydrogen ions. At the latter concentration, the effect of the enzyme is not impaired. A. McK.

Function of Peroxides in the Living Cell. VII. Chemical Nature of Oxydases. ROBERT CHODAT and ALEXIS BACH (*Ber.*, 1904, 37, 36—43. Compare *Abstr.*, 1903, i, 219, 378).—The fresh sap of *Lathræa squamaria*, which contains an oxydase, was acted on by a current of air and a 1 per cent. solution of barium hydroxide added drop by drop; a precipitate was produced which contained barium, gave the titanium reaction for hydrogen peroxide when decomposed with dilute sulphuric acid, and gave a blue coloration with starch and potassium iodide; no such effect was produced by stale sap which had lost its oxydase and become inactive, and it is suggested that the oxydase is simply an easily oxidisable substance which is converted into a peroxide by atmospheric oxygen. These peroxides are also produced in the living cell, and under the microscope with starch-iodide solutions thin sections show a blue coloration in the interior of the cell; this does not occur when the oxydase is absent, as tested, for instance, with guaiacum tincture, but the latter, being a more sensitive test, persists longer than the iodide reaction. The author cannot therefore accept Asō's conclusion, that the iodide reaction is produced by substances different from the oxydases.

The oxydases in some respects resemble nitrous acid, and a remarkable agreement is observed in the absorption of atmospheric oxygen by mixtures of nitrous acid and pyrogallol, and by oxydases mixed with pyrogallol, the presence of the nitrous acid and of the oxydase causing a great increase in the rate of absorption. Nitrous acid is, however, not present, and the purest oxydases contain very little albumin; oxydases prepared from moulds contain gummy substances, whilst Spitzer's preparations contain nucleo-proteids, but the active agent is probably independent of these associated materials.

T. M. L.

Manganese Salts as Oxydases in the presence of a Colloid. AUGUSTE TRILLAT (*Compt. rend.*, 1904, 138, 274—277. Compare this vol., i, 274).—A colloidal alkaline solution of a manganese salt exhibits properties which are strictly analogous to those of an oxydase, that is, it oxidises by acting as a carrier of atmospheric oxygen (compare Bertrand, *Abstr.*, 1897, ii, 493); such a solution is prepared by mixing a 3 per cent. solution of egg albumin with 0.02 gram of manganous chloride and a 0.1 per cent. solution of sodium or potassium carbonate, and has the following properties: (1) it rapidly oxidises from the surface downwards when exposed to the air, but without the formation of a precipitate; (2) it gives no colour reaction with guaiacum, until exposed to the air, when the blue colour rapidly develops (compare Gessard, *Abstr.*, 1903, i, 590); (3) it oxidises quinol to quinone and pyrogallol to purpurogallol (compare Bertrand, *Abstr.*, 1895, i, 386); (4) the fresh solution gives no coloration with tetramethyldiaminodiphenylmethane (absence of MnO_2), but the blue colour develops on exposure to the air (presence of MnO_2) and disappears on the addition of an oxidisable substance (reduction of MnO_2) (compare *Abstr.*, 1903, ii, 512); (5) the oxidation of phenolic compounds by the solution is accompanied by an evolution of carbon dioxide (compare Bertrand, *Abstr.*, 1895, i, 386); (6), the solutions lose their characteristic pro-

perties when heated to 105°. For example, fresh colloidal solutions of manganese in the presence of gallic acid absorbed 45, 38, and 47 volumes of oxygen respectively, whilst the oxygen absorbed by the same solutions, after boiling, were 0, 5, and 3 volumes respectively.

M. A. W.

Oxidation of Vanillin by the Oxydase of Mushrooms. R. LERAT (*Compt. rend. Soc. Biol.*, 1903, 55, 1325—1327).—Bourquelot observed the formation of a greyish-white, crystalline precipitate as the result of the action on vanillin of the oxydase obtained from various kinds of mushroom. The present research shows that this substance is identical with Tiemann's dehydrodivanillin. Morphine yields under similar conditions dehydromorphine (Bourquelot).

W. D. H.

Magnesium α -Naphthyl Bromide. SALOMON F. ACREE (*Ber.*, 1904, 37, 625—628).— α -Bromonaphthalene reacts readily with magnesium in presence of a trace of iodine or methyl iodide, forming crystalline *magnesium α -naphthyl bromide*, which is converted by carbon dioxide in ethereal solution into α -naphthoic acid, some naphthalene being also formed. Benzophenone and magnesium α -naphthyl bromide condense to form diphenyl- α -naphthylcarbinol, benzoyl chloride and magnesium α -naphthyl bromide form phenyl α -naphthyl ketone, but not phenyldi- α -naphthylcarbinol. Condensation also takes place with other ketones and aldehydes.

The foregoing carbinols dissolve in concentrated acids to intensely coloured solutions, from which water precipitates the original compound, this behaviour being probably due to the formation of quinonoid salts.

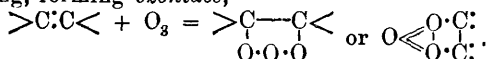
C. H. D.

Organic Chemistry.

Inflammation of Light Petroleum. GERHARD JUST (*Zeit. Elektrochem.*, 1904, 10, 202—204).—In washing woollen articles with light petroleum, the vapour frequently takes fire, usually when an article is being lifted out of the liquid. It has been shown by Richter that the inflammation is due to a spark discharge of a charge of electricity produced by the friction between the wool and the liquid, and that the fires are completely prevented by adding from 1/50 to 1/20 per cent. of magnesium oleate to the petroleum. The author shows that the effect of the addition is not due to any change in the dielectric constant of the light petroleum, but that it is due to an increase in its conductivity. A gold leaf electroscope is attached to an electrode dipping into light petroleum, another electrode dipping into the liquid being earthed; the electroscope under these conditions will retain a charge of electricity for several minutes. When a 1/20 per cent. solution of magnesium oleate is used, it is hardly possible to charge the electroscope at all.

Fires due to a similar cause have been observed in pouring ether into glass bottles. T. E.

Oxidising Action of Ozone. CARL D. HARRIES (*Ber.*, 1904, 37, 839—841. Compare *Abstr.*, 1903, i, 605, 807, 815; this vol., i, 15).—The nature of the reaction between ozone and unsaturated compounds depends on the presence or absence of water. In the absence of a solvent or in non-dissociating solvents, ozone is added at the double linking, forming *ozonides*,



In the presence of water, these ozonides are decomposed, forming ketones or aldehydes and hydrogen peroxide. It is possible that a small quantity of water may be sufficient to cause this decomposition, catalytic action taking place.

The ozonides are mostly highly explosive, but in some cases may be distilled under reduced pressure without decomposition. C. H. D.

$\beta\zeta$ -Dimethyl- $\Delta^{\beta:\epsilon}$ -heptadiene Diozonide. CARL D. HARRIES and RICHARD WEIL (*Ber.*, 1904, 37, 845—850).—Methylheptanone reacts with magnesium methyl iodide, forming ζ -hydroxy- $\beta\zeta$ -dimethyl- Δ^{β} -heptene [*aa*-trimethyl- Δ^{δ} -hexenol], $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{OH}$, a yellow oil boiling at 73—75° under 10.5 mm. pressure. It has a molecular refraction 44.72 and a sp. gr. at 20° 0.85496, n_D 1.45062 at 20°. Hydrogen bromide in acetic acid solution forms $\beta\zeta$ -dibromo- $\beta\zeta$ -dimethylheptane, crystallising from methyl alcohol in long needles and melting at 35°, converted by boiling with pyridine into $\beta\zeta$ -dimethyl- $\Delta^{\beta:\epsilon}$ -heptadiene, a colourless liquid of pleasant odour, which boils at 140—142° and does not form a crystallisable nitrosate or

tetrabromide. Ozone converts it, when moisture is excluded, into the *diozonide*, probably $\text{O} \begin{array}{c} \diagup \text{O} \cdot \text{CMe}_2 \\ \diagdown \text{O} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{O} \end{array} \begin{array}{c} \text{CMe}_2 \cdot \text{O} \\ \diagdown \text{O} \end{array} \text{O}$, a colourless, viscous, highly explosive oil.

The dimethylheptenol described above is converted into *cyclogeraniolene* by boiling with phosphoric acid. Ozone forms an oily *ozonide*, $\text{C}_9\text{H}_{16}\text{O}_4$, having a sp. gr. at 20° 1.0983, n_D 1.46509 at 17° ; the molecular refraction is 47.33. It boils at $80\text{--}100^\circ$ under 10 mm. pressure, yielding a less viscous distillate. The constitution is unknown, four oxygen atoms having been added instead of three.

All these ozonides are decomposed violently by concentrated sulphuric acid, decolorise indigo solution, decompose potassium iodide, and form hydrogen peroxide with water. C. H. D.

Melting Points of Solid Chloroform, Toluene, and Ether. EBENEZER H. ARCHIBALD and DOUGLAS MCINTOSH (*J. Amer. Chem. Soc.*, 1904, 26, 305—306).—The melting points of pure chloroform, toluene, and ether were determined by means of the hydrogen thermometer, the results being corrected by Travers' method (Abstr., 1903, ii, 9). The following are the melting points obtained: chloroform, -63.2° ; ether, -117.6° ; toluene, -97° to -99° . E. G.

Electrolytic Preparation of Iodoform from Acetone. JOHN E. TEEPLE (*J. Amer. Chem. Soc.*, 1904, 26, 170—177).—A nearly theoretical yield of iodoform can be obtained by the electrolysis of a neutral solution of potassium iodide in presence of acetone, without the use of a diaphragm. The alkali produced must be neutralised as fast as it is formed; this may be effected by means of carbon dioxide, hydrochloric acid, hydriodic acid, or iodine. The temperature should not be allowed to rise above 25° , and the solution should be kept well stirred. A comparatively low anode current density and a high cathode density are required.

For a continuous process, it is probable that it would be best to neutralise the alkali by means of iodine. It was found by experiment that the yield is gradually decreased owing to the accumulation of potassium acetate, but that when the potassium acetate in the solution amounts to as much as 12 per cent., the yield of iodoform is not diminished by more than 15 per cent. E. G.

Derivatives of the Amyl Alcohols from Fusel Oil. IV. WILLY MARCKWALD (*Ber.*, 1904, 37, 1038—1052).—Details are given for preparing pure active amyl alcohol from fusel oil by first removing a large proportion of the inactive alcohol by taking advantage of its ready conversion by hydrogen chloride into amyl chloride, and subsequently working up the enriched product with 3-nitrophthalic acid (compare Abstr., 1901, i, 248).

A ready separation of the two alcohols cannot be effected by converting the mixture into the corresponding mixed urethanes and recrystallising the product, because the *d*-amylurethane dissolves in the *iso*amylurethane, forming mixed crystals; the converse, however,

is not true, as the *iso*amyl compound is only absorbed sparingly by the active urethane. Pure *d*-amylurethane melts at 61° and has $[\alpha]_D + 3.32^{\circ}$ in benzene solution; the pure *iso*amylurethane melts at 64.5° .

A systematic study has been made of the solubility of mixed crystals of the two barium amyl sulphates, which shows that a continuous increase of solubility accompanies an increase in the percentage of active salt; the curve connecting these quantities is parabolic.

d-Amyl alcohol, on oxidation, gives pure *d*-valeric acid having $\alpha_D + 8.75^{\circ}$ for $l = 0.5$. *d*-Amyl iodide cannot be obtained pure by the action of phosphorus iodide on the alcohol (compare Klages and Sautter, this vol., i, 302), as partial racemisation occurs; it is prepared therefore from hydrogen iodide and the alcohol. The following values show its rotatory dispersion: red, $\lambda 665.9$, $[\alpha] + 4.42^{\circ}$; yellow, $\lambda 588.0$, $[\alpha] + 5.64^{\circ}$; green, $\lambda 533.0$, $[\alpha] + 6.89^{\circ}$; blue, $\lambda 488.5$, $[\alpha] + 8.20^{\circ}$; dark blue, $\lambda 448.2$, $[\alpha] + 9.86^{\circ}$; it has a sp. gr. 1.524 at $20^{\circ}/4^{\circ}$. *d*-Amyl bromide boils at $118-120^{\circ}$ and has a sp. gr. 1.221 at $20^{\circ}/4^{\circ}$ and $[\alpha]_D + 3.68^{\circ}$ at 20° . Pure *d*-methylethylpropylmethane [β -ethylpentane] (compare Just, Abstr., 1884, 169; Welt, Abstr., 1895, ii, 97) boils at $90-92^{\circ}$ and has a sp. gr. 0.6865 at $20^{\circ}/4^{\circ}$ and $[\alpha]_D + 9.5^{\circ}$ at 20° .

Pure *iso*amylphthalimide, on cooling, solidifies and then melts at 12.5° (compare Neumann, Abstr., 1890, 890). *d*-Amylphthalimide, prepared from *d*-amyl bromide and potassium phthalimide, melts at 23° , boils at 303° , and, when liquid, has a sp. gr. 1.0930 at $25^{\circ}/4^{\circ}$; it has $[\alpha]_D + 7.53^{\circ}$ at 25° . *d*-Amylphthalamic acid crystallises from benzene in white leaflets, melts at 123° , and, on hydrolysis with 10 per cent. sodium hydroxide solution, gives *d*-amylamine, which boils at $95.5-96^{\circ}$, has a sp. gr. 0.7505 at $25^{\circ}/4^{\circ}$, and $[\alpha]_D - 5.86^{\circ}$ at 25° ; the *platinochloride* of the base decomposes at 240° . The *hydrochloride* is hygroscopic, melts at 176° , and is inactive in solution, although racemisation has not occurred; this is shown by the pure active base being liberated by the addition of alkali.

Pure *d*-amyl phenylcarbamate, prepared from pure *d*-amyl alcohol and phenylcarbimide, forms white crystals, melts at 30° , and, in chloroform, has $[\alpha]_D + 6.4^{\circ}$ ($c = 5$) and $+ 6.6^{\circ}$ ($c = 15$); Goldschmidt and Freund's *d*-amyl phenylcarbamate (Abstr., 1894, ii, 405), although melting at the same temperature, had $[\alpha]_D = 4.19^{\circ}$, and contained only 65 per cent. of the active ester. *iso*Amyl phenylcarbamate, prepared from *iso*amyl alcohol, melts at 55° . A melting point curve is given for mixtures of *d*- and *iso*-amyl phenylcarbamates. W. A. D.

Pentane- $\beta\delta$ -diol and $\beta\delta$ -Dibromopentane. A. PORAY-KOSCHITZ (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 1112-1116).—Pentane- $\beta\delta$ -diol, $C_5H_{12}O_2$, prepared by reducing methyl β -hydroxypropyl ketone in aqueous solution by means of 3 per cent. sodium amalgam, is a colourless, viscous liquid, stable in the air and soluble in water and organic solvents; it boils at 197° under the ordinary pressure, and at $90-92^{\circ}$ under 10 mm. pressure, and has the sp. gr. 0.96607 at $0^{\circ}/0^{\circ}$. Its *diacetyl* derivative, $C_9H_{16}O_4$, is a colourless liquid, which boils at 84° under 8 mm. pressure and boils and decomposes at $200-210^{\circ}$ under the ordinary pressure.

βδ-Dibromopentane, $C_5H_{10}Br_2$, prepared by the action of hydrobromic acid on pentane-2:4-diol in a sealed tube, boils at 63.5° under 9 mm. pressure, and has the sp. gr. 1.6789 at $0^\circ/0^\circ$. T. H. P.

Monocarbon Compounds. Methylene Hydroxybromide. LOUIS HENRY (*Rec. trav. chim.*, 1904, 23, 16—25. Compare Favre, Abstr., 1895, i, 14, and Littarscheid, Abstr., 1901, i, 443).—In a previous communication (*Bull. Acad. roy. Belg.*, 1893, 615), the author has stated that the principal product of the action of hydrogen bromide on formaldehyde is methylene hydroxybromide (bromomethyl alcohol). He is now of opinion that this product is the hydrobromide of dimethyl ether, analogous in constitution to the hydrochloride described by Friedel (this Journ., 1875, 1245). T. A. H.

Preparation of the Lower Halogen-methyl Alkyl Ethers. FRANZ M. LITTELSCHIED (*Annalen*, 1903, 330, 108—112. Compare Abstr., 1901, i, 443).—A method of preparing the halogen-methyl alkyl ethers, $CH_2Cl \cdot OR$, is described, which has advantages over that devised by Wedekind (D.R.-P., 1901, 135310). Molecular quantities of the alcohol and trioxymethylene (the former in slight excess) are mixed, and hydrogen chloride passed in until a liquid is obtained consisting of two layers; the lower is a saturated solution of hydrogen chloride, and the upper contains the halogenated ether. After addition of calcium chloride to remove alcohol, the latter is distilled, a yield of 85—95 per cent. being obtained. K. J. P. O.

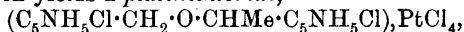
Dichloromethyl Ether. FRANZ M. LITTELSCHIED (*Annalen*, 1903, 330, 112—117. Compare preceding abstract).—The *s*-dichloromethyl ether was prepared from the monochloromethyl ether (see preceding abstract) by passing a slow stream of dry chlorine for about 40 hours through the ether, which was kept at 12° in a place shaded from the light. The ether boiled at 103 — 106° .

When the dichloromethyl ether and pyridine are brought together in the presence of dry ether, a semi-crystalline mass separates, which can be converted into a *platinichloride*, $(C_5NH_5Cl \cdot CH_2)_2O \cdot PtCl_4$; the latter crystallises in large, reddish-yellow leaflets melting at 235° .

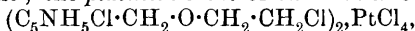
Strychnine forms a similar compound with dichloromethyl ether, the *platinichloride*, $(C_{21}H_{22}O_2N_2 \cdot CH_2Cl)_2O \cdot PtCl_4$, of which forms a pale yellow powder decomposing at 240° . The *aurichloride* was obtained from the platinichloride, and crystallises in yellowish-brown needles, becoming coloured at 215° and melting at 220° . K. J. P. O.

Chlorination of Chloromethyl Ethyl Ether. FRANZ M. LITTELSCHIED (*Annalen*, 1903, 330, 118—131. Compare preceding abstracts).—Chloromethyl ethyl ether, prepared by the action of hydrogen chloride on a mixture of trioxymethylene and ethyl alcohol, was treated with dry chlorine for about 100 hours in diffused daylight, and the product fractionated; four fractions were obtained, (i) b. p. 112 — 114° , (ii) b. p. 144 — 148° , (iii) b. p. 174 — 176° , and (iv) b. p. 205° . Fraction (i) contains the dichloride, $CH_2Cl \cdot O \cdot CHCl \cdot CH_3$, since when heated with water it yields acetaldehyde and immediately gives up all its

chlorine to aqueous silver nitrate. Further, it reacts with pyridine in the proportion of 1 mol. of pyridine to 2 mols. of ether, forming a compound which yields a *platinichloride*,

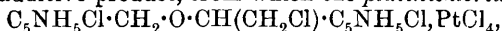


crystallising in microscopic plates melting and decomposing at 205° ; the *aurichloride* melts at 178° . The dichloro-compound prepared by Henry (Abstr., 1895, i, 80) is the isomeride. It yields only one atom of chlorine when treated with silver nitrate, and combines only with 1 mol. of pyridine; the *platinichloride* of this additive product,



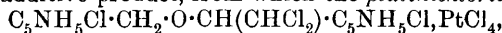
crystallises in golden-yellow leaflets melting at 162° , the *aurichloride* forms lustrous, prismatic crystals melting at 84° .

Fraction (ii) is the compound $\text{CH}_2\text{Cl}\cdot\text{O}\cdot\text{CHCl}\cdot\text{CH}_2\text{Cl}$, since two atoms of chlorine can be eliminated by silver nitrate. With pyridine, it forms an additive product, from which the *platinichloride*,



can be obtained in microscopic leaflets melting at 212° ; the *aurichloride* forms microscopic crystals melting at 212° .

Fraction (iii) is the trichloride, $\text{CH}_2\text{Cl}\cdot\text{O}\cdot\text{CHCl}\cdot\text{CHCl}_2$; with pyridine, it yields an additive product, from which the *platinichloride*,



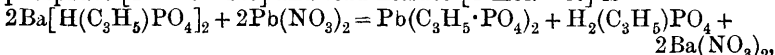
is obtained as a microcrystalline, yellowish-red powder melting at 224° .

Fraction (iv) was too small for accurate investigation; it consisted mainly of a tetrachloride.

K. J. P. O.

Silver and Lead Salts of Alkyl Dihydrogen Phosphates.

JACQUES CAVALIER (*Compt. rend.*, 1904, 138, 762—763. Compare Abstr., 1900, i, 579; 1901, ii, 502, and Berthelot, Abstr., 1901, ii, 502, 503).—In respect of the solubility and stability of their lead and silver salts, ethyl and allyl dihydrogen phosphates closely resemble phosphoric acid, the normal salt being precipitated by lead or silver nitrate from a solution, neutral to methyl-orange, of the barium hydrogen alkyl phosphate, whilst the liquid becomes acid to the same indicator; the lead or silver hydrogen alkyl phosphates can only be formed in a strongly acid solution. The equation representing the formation of lead allyl phosphate from barium hydrogen allyl phosphate [1 mol. = 10*l*] and lead nitrate [1 mol. = 5*l*] is



but the reaction is not complete, only about four-fifths of the theoretical quantity of the lead salt being formed. A yield of 52 per cent. of lead ethyl phosphate is obtained with solutions of similar concentration at the boiling point. The silver salts of ethyl and allyl dihydrogen phosphates are much more soluble than the corresponding lead salts, only 4 per cent. of the theoretical quantity of silver ethyl phosphate, Ag_2EtPO_4 , being obtained from concentrated solutions of barium hydrogen ethyl phosphate [$\text{Ba}(\text{EtHPO}_4)_2 = 2*l*$] and silver nitrate [$2\text{AgNO}_3 = 2*l*$].

M. A. W.

Barium and Lead Uranyl Acetates. JOSEF ZEHENTER (*Monatsh.*, 1904, 25, 197—219).—See this vol., ii, 344.

Marckwald's Asymmetric Synthesis of Active Valeric Acid. JULIUS B. COHEN and THOMAS S. PATTERSON (*Ber.*, 1904, 37, 1012—1014).—A criticism of Marckwald's views (compare this vol., i, 221). W. A. D.

Some Derivatives of Racemic α -Campholytic and α -Campholenic Acids. GUSTAVE BLANC and L. DESFONTAINES (*Compt. rend.*, 1904, 138, 696—697).—A racemic campholytonitrile, boiling at 200—205°, can be obtained from the corresponding amide and phosphorus pentachloride; a dichloro-compound, $C_8H_{13} \cdot CCl_2 \cdot NH_2$, which melts and partially sublimes at 175°, is also produced in this reaction. The nitrile so obtained is not pure, for on saponification it gives [as well as the original racemic campholytamide (melting at 103°)] an amide which melts at 171—172°. Campholytonitrile can be reduced with sodium and ethyl alcohol to an unsaturated base, $C_8H_{13} \cdot CH_2 \cdot NH_2$, which boils at 184—185° and is insoluble in water, but dissolves readily in ordinary organic media. For the sake of comparison, *r*- α -aminocampholene, was prepared. It was obtained by the following steps: (1) dehydration of *r*-camphoroxime to *r*- α -campholenonitrile, $C_8H_{13} \cdot CH_2 \cdot CN$, which boils at 228°; (2) saponification of this nitrile to *r*- α -campholenamide, which melts at 122° and gives (3), with bromine and sodium hydroxide, *r*- α -aminocampholene, $C_8H_{13} \cdot CH_2 \cdot NH_2$, which boils at 184°. The oxamide of this base, $C_2O_2(NH \cdot C_9H_{15})_2$, melts at 134°, and the carbamide derivative, $NH_2 \cdot CO \cdot NH \cdot C_9H_{15}$, at 115—116°. The corresponding derivatives furnished by the base obtained from *r*- α -campholytic nitrile are difficult to purify, the oxamide melts at 125°, and the carbamide at 112°. It is, however, probable that the two bases are identical, and that the slight differences are due to the latter compounds not being quite pure. S. S.

Action of Dehydrating Agents on Hydroxypivalic Acid [β -Hydroxy- $\alpha\alpha$ -dimethylpropionic Acid]. EDMOND E. BLAISE and L. MARCILLY (*Bull. Soc. chim.*, 1904, [iii], 31, 308—317).—When β -hydroxy- $\alpha\alpha$ -dimethylpropionic acid, $OH \cdot CH_2 \cdot CMe_2 \cdot CO_2H$ (this vol., i, 219), is heated alone at 200° or is warmed with a 60 per cent. solution of sulphuric acid or with hydrochloric or hydrobromic acids (in this case a small quantity of bromopivalic acid is also formed), it is converted into a series of anhydrides of which the principal is a *product* ("hemipoly lactide") for which the formula

$OH \cdot CH_2 \cdot CMe_2 \cdot CO_2 \cdot [CH_2 \cdot CMe_2 \cdot CO_2]_4 \cdot CH_2 \cdot CMe_2 \cdot CO_2H$, is suggested. This substance forms white, microscopic needles, softens at 158°, and melts at 165°. It is nearly insoluble in most solvents, but dissolves in phenol and in boiling formic and acetic acids. When treated with solutions of potassium hydrogen carbonate or ammonia, it is converted into the respective salts, which are insoluble in water. When β -hydroxy- $\alpha\alpha$ -dimethylpropionic acid is heated at 250—270°, it decomposes forming water, formaldehyde, isobutyric acid, isobutylene, and carbon monoxide and dioxide. The first two substances are regarded as produced by the direct decomposition of the acid, and the others, with the exception of the carbon monoxide, as due to the

gradual degradation of the hemipoly lactide first formed. A scheme illustrating the course of this decomposition is given in the original.

T. A. H.

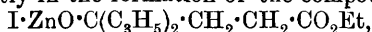
***αα*-Methylethylhydracrylic Acid.** EDMOND E. BLAISE and L. MARCILLY (*Bull. Soc. chim.*, 1904, [iii], 31, 317—325).—Ethyl *α*-bromomethylethylacetate (Auwers and Fritzweiler, *Abstr.*, 1898, i, 126), prepared by brominating the acid chloride and treating the resulting product with alcohol, was converted into *ethyl αα*-methylethylhydracrylate, $\text{OH}\cdot\text{CH}_2\cdot\text{CMeEt}\cdot\text{CO}_2\text{Et}$, by the general method already described (this vol., i, 218). This is a mobile liquid of pleasant odour; it boils at 108° under 25 mm. pressure. The *acetyl* derivative, obtained by acetylating the ester with acetyl chloride, boils at 113° under 20 mm. pressure.

αα-Methylethylhydracrylic acid crystallises from a mixture of ether and light petroleum, melts at 56° , is odourless, and dissolves in water and alcohol; the *potassium* salt crystallises from alcohol and melts at 262° , and the *phenylurethane*, $\text{NHPh}\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CMeEt}\cdot\text{CO}_2\text{H}$, separates from boiling water in slender needles, melts at 114 — 115° , and is soluble in alcohol. The acid, when oxidised with chromic acid, furnishes methylethylmalonic acid (m. p. 118°) and small quantities of *α*-methylbutaldehyde and carbon dioxide.

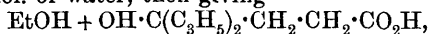
Quinine αα-methylethylhydracrylate separates from boiling water in slender, slightly yellow needles, melts at 177° , and dissolves in alcohol and benzene. This salt was fractionally crystallised from boiling water, but no separation into optical isomerides was thereby effected, the apparently least and most soluble fractions having $[\alpha]_D - 124^\circ 10'$ and $-124^\circ 15'$ respectively. The *cinchonine* salt crystallises from benzene in slender needles, melts at 121 — 122° , and re-melts at 255° . When fractionally crystallised from benzene, the apparently least and most soluble fractions had $[\alpha]_D + 130^\circ 30'$ and $+130^\circ 36'$ respectively. The acid regenerated from the apparently least soluble fractions of the two salts was optically inactive. Attempts are now being made to deracemise the acid by the action of moulds.

T. A. H.

Action of Ethyl Succinate on Allyl Iodide in presence of Zinc. Synthesis and Properties of *γ*-Diallylbutyrolactone. ALEXANDER KASANSKY (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 1179—1188).—The action of ethyl succinate on allyl iodide in presence of zinc results firstly in the formation of the compound



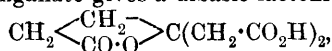
which then undergoes change in two directions: (1) with 1 mol. of water it yields $\text{I}\cdot\text{Zn}\cdot\text{OH} + \text{OH}\cdot\text{C}(\text{C}_3\text{H}_5)_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, the latter, with another mol. of water, then giving



that is, *γ*-hydroxy-*γγ*-diallylbutyric acid, which was characterised by means of its *barium* and *calcium* salts. (2) It loses a molecule of

water, yielding *γγ*-diallylbutyrolactone, $\text{CH}_2\left\langle\begin{smallmatrix}\text{CH}_2 \\ \text{CO}\cdot\text{O}\end{smallmatrix}\right\rangle\text{C}(\text{C}_3\text{H}_5)_2$, which is a viscous liquid decomposed by water, but readily soluble in alcohol

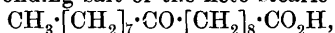
or ether; it boils at 266—267°, and, under the action of an alkali or alkaline earth hydroxide, yields the corresponding salts of γ -hydroxy- $\gamma\gamma$ -diallylbutyric acid. With bromine, it forms an additive compound, $C_{10}H_{14}O_2Br_4$, which crystallises from alcohol in long, rectangular plates and melts and decomposes slightly at 125—127°. With hydrogen iodide, it gives γ -iodo- $\gamma\gamma$ -diallylbutyric acid, $Cl(C_3H_5)_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$, which is obtained as a viscous, red liquid. Reduction of this iodo-acid by means of sodium amalgam in alcoholic solution yields $\gamma\gamma$ -diallylbutyric acid, $CH(C_3H_5)_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$, which boils at 264—267°; its *sodium* and *silver* salts were prepared and analysed; with bromide, it yields a tetrabromo-additive compound, which gradually loses hydrogen bromide, forming a lactonic derivative containing 3 atoms of bromine. Oxidation of $\gamma\gamma$ -diallylbutyrolactone by means of potassium permanganate gives a dibasic lactonic acid,



of which the *calcium* salt was prepared.

T. H. P.

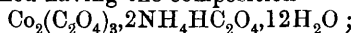
Behaviour at High Temperatures of Salts of the Dihydroxystearic Acid obtained by the Oxidation of Oleic Acid by Alkaline Potassium Permanganate Solution. NICOLAUS SAYTZEFF and ALEXANDER M. SAYTZEFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 1193—1197).—On heating the calcium salt of θ -dihydroxystearic acid, $CH_3 \cdot [CH_2]_7 \cdot CH(OH) \cdot CH(OH) \cdot [CH_2]_7 \cdot CO_2H$, at 170° or the zinc salt at 185°, the corresponding salt of the keto-stearic acid,



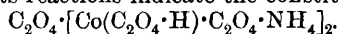
prepared by Baruch (*Abstr.*, 1894, i, 170), is obtained. The same acid, of which the *sodium*, *barium*, and *silver* salts were prepared and analysed, may be obtained by heating θ -dihydroxystearic acid with zinc chloride at 140°.

T. H. P.

New Salts of Tervalent Cobalt and of Quadrivalent Uranium. N. A. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 1247—1249).—On dissolving freshly-precipitated and washed cobalt hydroxide in a mixture of solutions of oxalic acid and ammonium oxalate, a green double salt is obtained having the composition

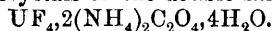


it may be purified by dissolving in 30 per cent. alcohol, 50 per cent. methyl alcohol or water, and precipitating it from solution by means of strong alcohol or ether. It forms dark green plates or prisms, giving a bright green solution. Alkali hydroxides, barium hydroxide or carbonate, nitrous acid, potassium thiocyanate, potassium dichromate, or ferricyanide, or tannin are without action on solutions of the salt in the cold. Its reactions indicate the constitution



No similar salt of nickel could be prepared.

On dissolving uranium tetrafluoride in solutions of ammonium oxalate, a dark green liquid is obtained, which shows a violet fluorescence and deposits crystals of the double salt,



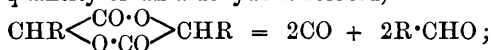
T. H. P.

Diethylisosuccinic Acid. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and F. PERRIN (*Bull. Soc. chim.*, 1904, [iii], 31, 350—351).—*Ethyl diethylisosuccinate*, $\text{CHEt}_2 \cdot \text{CH}(\text{CO}_2\text{Et})_2$, prepared by the action of ethyl malonate on γ -iodopentane, CHEt_2I , in presence of sodium ethoxide dissolved in alcohol, is a liquid which boils at 242—245°. The corresponding *acid* crystallises in large, transparent tablets and melts at 52—53°; the *anilide* forms small, colourless needles melting at 219—220°. T. A. H.

Synthesis of *aa*-Dimethylglutaric Acid and of *aa*-Dimethyladipic Acid. GUSTAVE BLANC (*Compt. rend.*, 1904, 138, 579—580).—*aa*-Dimethyl- γ -butyrolactone, $\text{CH}_2 \begin{smallmatrix} \text{CMe}_2 \cdot \text{CO} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{O}$, can be obtained by reducing ethyl *aa*-dimethylsuccinate with sodium and absolute alcohol. This lactone boils at 201—202° under atmospheric pressure, and, when heated in sealed tubes with dry potassium cyanide for 5 hours at 270°, yields a product, evidently potassium γ -cyano-*aa*-dimethylbutyrate, which may be hydrolysed to *aa*-dimethylglutaric acid melting at 85°. The synthetical product is identical with that obtained from *isolauronic* acid by oxidation.

Similarly, ethyl *aa*-dimethylglutarate gives *aa*-dimethyl- δ -valerolactone, $\text{CH}_2 \begin{smallmatrix} \text{CMe}_2 \cdot \text{CO} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{O}$, which boils at 105° under 13 mm. pressure and furnishes a barium salt crystallising with $1\frac{1}{2}\text{H}_2\text{O}$. This lactone, by treatment with potassium cyanide and subsequent hydrolysis, yields *aa*-dimethyladipic acid melting at 85—87°, and identical with the dimethyladipic acid already prepared from β -ionone or dihydroiselauroic acid. From these reactions, it is evident that the reduction of *aa*-dimethylsuccinic and glutaric esters involves the carboxyl group attached to the primary carbon atom. S. S.

A Method of Preparing Aldehydes and Systematically Degrading Acids. EDMOND E. BLAISE (*Compt. rend.*, 1904, 138, 697—699).—When a lactide is distilled, decomposition ensues, and a considerable quantity of an aldehyde is formed,



at the same time, a small amount of an unsaturated acid is produced, $\text{CH}_2\text{R} \cdot \text{CH} \begin{smallmatrix} \text{CO} \cdot \text{O} \\ \text{O} \cdot \text{CO} \end{smallmatrix} \text{CH} \cdot \text{CH}_2\text{R} = 2\text{R} \cdot \text{CH} : \text{CH} \cdot \text{CO}_2\text{H}$. The aldehyde can be isolated from the distillate by fractionation; the yield varies from 50—60 per cent. of the theoretical. This reaction affords a means of degrading the fatty acids, the complete process involves four steps: (1) preparation of the α -monobromo-derivative, (2) replacement of bromine by hydroxyl, (3) heating the α -hydroxy-acid to obtain the lactide and distillation of the latter, (4) oxidation of the aldehyde to the corresponding acid. This process was carried out with hexoic, pelargonic, lauric, myristic, and palmitic acids. The following substances are described: *α -bromopelargonic acid* is a liquid; its *ethyl ester* boils at 138—140° under 24 mm. pressure. *α -Hydroxypelargonic acid* crystallises in plates, melts at 70°, and gives an *anilide* melting

at 69—70°, and an *ethyl* ester melting at 23—24°. *α-Acetoxy-pelargonic acid* is a liquid boiling and decomposing slightly at 171—174° under 10 mm. pressure. The aldehydes prepared are: *n-valeraldehyde* from hexoic acid, which gives an oxime melting at 52°; *n-octaldehyde*, from pelargonic acid, a liquid, which boils at 81° under 32 mm. pressure, and furnishes an oxime melting at 58—59°, a *phenylhydrazone*, which melts at 101°, and a diethylacetal, which boils at 221—223°. *Tridecanal*, from myristic acid, is a solid, which distills at 152° under 24 mm. pressure, and *n-pentadecanal*, from palmitic acid, is also a solid, which boils at 185° under 25 mm. pressure. S. S.

Action of Calcium Hydroxide on *iso*Butaldehyde. PETER HERRMANN (*Monatsh.*, 1904, 25, 188—196).—Lime water brings about the condensation of *isobutaldehyde* at the ordinary temperature to *isobutaldol*, $C_8H_{16}O_2$, together with traces of *isobutyric acid*. When milk of lime is employed, heat is developed and the condensation product contains, in addition to *isobutaldol*, octoglycol *isobutyrate*, $C_{12}H_{24}O_3$, which is identified by hydrolysis to octoglycol and *isobutyric acid*. The latter compounds are also found in small quantity in the condensation product, partial hydrolysis of the ester having taken place. The same products are obtained, with the addition of *isobutyl alcohol*, on heating *isobutaldehyde* with calcium hydroxide under pressure. C. H. D.

Synthetic *iso*Valeraldehyde and its Condensation Products. M. CIHLAR (*Monatsh.*, 1904, 25, 149—158).—The occurrence of the *isovalerate* of a glycol, $C_{10}H_{22}O_2$, in the condensation products of *isovaleraldehyde* with alkali, observed by Kohn (*Abstr.*, 1896, i, 461; 1897, i, 396) and Rosinger (*Abstr.*, 1901, i, 669), is contrary to the general rule given by Lieben (*Abstr.*, 1896, i, 403). The aldehyde employed was prepared from fermentation amyl alcohol, and the formation of the ester is due to the presence of a certain quantity of γ -methylbutaldehyde.

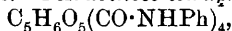
Pure *isovaleraldehyde* may be synthetically prepared from *isobutyl iodide* by conversion into the cyanide, hydrolysis, conversion into the calcium salt, and distillation of a mixture of the calcium *isovalerate* and calcium formate. Or the *isovaleric acid* may be prepared by heating *isopropylmalonic acid* at 160—180°, and the calcium salt then distilled in the same way. The aldehyde boils at 92.5°. The *oxime* boils at 161.3° under 759 mm. pressure, and is converted by acetic anhydride into the *nitrile*, boiling at 129.2—130° under 743 mm. pressure.

When treated with alcoholic potassium hydroxide or dry potassium carbonate, *isovaleraldehyde* condenses, yielding α -*isopropyl*- β -*isobutyl*-acraldehyde, $CHMe_2 \cdot CH_2 \cdot CH : C(CHO) \cdot CHMe_2$; no glycol ester is produced. C. H. D.

The Alkyl Allyl and Propenyl Ketones. EDMOND E. BLAISE (*Compt. rend.*, 1904, 138, 636—638. Compare this vol., i, 290).—The normal product of the condensation of allyl iodide and an alkyl nitrile is the alkyl ketone ($CH_2 : CH \cdot CH_2 \cdot COR$), the propenyl ketone ($CH_3 \cdot CH_2 : CH \cdot COR$), which is always present in the final product, being formed from the

former by an intramolecular change brought about by the action of sulphuric acid. The same change is effected readily by the halogen acids at the ordinary temperature, and even at -80° in the case of hydrobromic acid, the final product being the corresponding alkyl β -bromopropyl ketone, $\text{CH}_3\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{COR}$. A similar change occurs when the alkyl allyl ketone is heated with 10 per cent. solution of sulphuric acid, the product consisting of the alkyl propenyl ketone and the alkyl β -hydroxypropyl ketone, $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{COR}$. Owing to the readiness with which the alkyl allyl ketone is converted into the isomeric propenyl derivative, all attempts to prepare derivatives of the former by replacing the hydrogen atoms of the methylene group situated between the carbonyl radicle and ethylenic carbon atom have been unsuccessful; sodium ethoxide gives the corresponding β -ethoxypropyl ketone, $\text{CH}_3\cdot\text{CH}(\text{OEt})\cdot\text{CH}_2\cdot\text{COR}$, and formaldehyde in the presence of piperidine (compare Knoevenagel, *Abstr.*, 1902, i, 226; 1903, i, 638) gives the isomeric propenyl ketone. M. A. W.

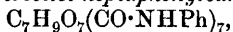
The Phenylcarbamates of Sugars. LÉON MAQUENNE and W. GOODWIN (*Compt. rend.*, 1904, 138, 633—636).—Tesmer (*Abstr.*, 1885, 774; 1886, 49) showed that phenylcarbimide reacted with polyhydric alcohols belonging to the mannitol and sucrose series to give sparingly soluble phenylcarbamates. The authors have prepared similar compounds from some pentoses, hexoses, heptoses, and several polyoses by boiling the sugar with about $1\frac{1}{4}$ times the theoretical quantity of phenylcarbimide dissolved in two or three times its volume of dry piperidine. The compounds thus prepared are amorphous or microcrystalline, very sparingly soluble in the ordinary solvents, and have no sharp melting point, but decompose with evolution of a gas having the odour of phenylcarbimide. *l*-Arabinose tetraphenylcarbamate,



is a white, amorphous powder, insoluble in water, very slightly soluble in alcohol, and decomposes at about 250 — 255° . *l*-Xylose tetraphenylcarbamate is isomeric with the preceding compound and even less soluble in alcohol, and melts at about 265 — 270° . *d*-Dextrose pentaphenylcarbamate, $\text{C}_6\text{H}_7\text{O}_6(\text{CO}\cdot\text{NHPh})_5$, is an amorphous powder very slightly soluble in boiling alcohol and melts at about 255° . *d*-Galactose pentaphenylcarbamate is amorphous, slightly soluble in hot alcohol, and decomposes at 275° . *Lactose* octophenylcarbamate, $\text{C}_{12}\text{H}_{14}\text{O}_{11}(\text{CO}\cdot\text{NHPh})_8$, melts at about 275 — 280° and does not reduce Fehling's solution even after boiling with dilute sulphuric acid. *Trehalose* octophenylcarbamate is amorphous and melts at about 283° . *Melezitose* undecaphenylcarbamate, $\text{C}_{18}\text{H}_{21}\text{O}_{16}(\text{CO}\cdot\text{NHPh})_{11}$, is an amorphous powder melting at about 180° and slightly soluble in warm alcohol.

Contrary to Tesmer's experience, the authors find that the polyhydric alcohols give derivatives with phenylcarbimide in which each hydroxyl of the original compound is replaced by a carbamate residue, and the following compounds were prepared. *Mannitol* hexaphenylcarbamate, $\text{C}_6\text{H}_8\text{O}_6(\text{CO}\cdot\text{NHPh})_6$, melting at about 303° , is a powder consisting of very fine needles. From 100 parts of the sugar, 494 parts of the carbamate were obtained, theory requires 492.

Dulcitol hexaphenylcarbamate melts at 315° and closely resembles the preceding compound. *Perseitol heptaphenylcarbamate*,



melts at 297° and is insoluble in boiling alcohol; 100 parts of the sugar yield 491 parts of the carbamate, the amount required by theory being 493.

Ethylcarbimide reacts with mannitol to yield a compound melting at 270° and containing the proportion of nitrogen required for a hexaethylcarbamate. M. A. W.

Condensation of Dextrose by Fusion with Ammonium Chloride. HUGO F. KLATT (*Annalen*, 1903, 329, 350—362).—After an historical *résumé* of the attempts to prepare synthetical dextrins (glucosins) from dextrose, an account is given of the dextrins obtained by heating dextrose with ammonium chloride.

An intimate mixture of anhydrous dextrose and 1 per cent. ammonium chloride was heated for varying times at 120 — 130° , and the product fractionated by dissolving in water and precipitating with alcohol; the earlier fractions were free from dextrose; the material was completely soluble in water, gave no phenylhydrazone or osazone with phenylhydrazine or *p*-bromophenylhydrazine, and no coloration with iodine, but readily reduced Fehling's solution (reducing power 10.1 about) and ammoniacal silver nitrate. The aqueous solution showed no mutarotation, and had $[\alpha]_D$ 94 — 100° . Analysis gave numbers closely agreeing with the formula $(\text{C}_6\text{H}_{10}\text{O}_5)_3\cdot\text{H}_2\text{O}$, but mol. weight determinations by the freezing point method pointed rather to the formula $(\text{C}_6\text{H}_{10}\text{O}_5)_4\cdot\text{H}_2\text{O}$. The most sparingly soluble fractions, which underwent no further change on fractionation, had $[\alpha]_D$ 105 — 106° and a reducing power of 10. The material did not ferment with yeast, nor was it attacked by diastase; by dilute acids, it was easily hydrolysed, forming dextrose; on oxidation with nitric acid, *d*-saccharic acid was alone produced. It is very doubtful if even the final fractions were exclusively composed of a single individual substance. The material appears to resemble closely, but does not seem to be identical with, the glucosins described by Grimaux (*Abstr.*, 1886, 1003). K. J. P. O.

Glutamine. EUGÈNE SELLIER (*Chem. Centr.*, 1904, i, 789—790; from *Bull. Assoc. Chim. Sucr. Dist.*, 21, 754—760).—Glutamine has been isolated from the juice of the sugar beet; it is readily soluble in water at the ordinary temperature, less so in water at 0° , and only slightly so in alcohol. It is precipitated from its aqueous solution by alcohol in the form of very small, slender needles, which are occasionally grouped in star-shaped aggregates. After remaining for a few minutes with Nessler's reagent, glutamine gives the ammonia reaction.

Glutamine behaves as a very weak acid towards indicators, the acidity shown by phenolphthalein and rosolic acid increasing as the temperature rises, whilst with litmus and resazurine, temperature has no effect on the acidity. When distilled in a vacuum with lime at 36 — 40° , it loses a portion of its nitrogen in the form of ammonia, but under similar conditions magnesium oxide and barium carbonate do not cause liberation of ammonia. Glutamine has $[\alpha]_D +6.15^{\circ}$ at 20°

in a 1 per cent. aqueous solution. The rotatory power is decreased by the addition of normal lead acetate, whilst basic lead acetate causes it to become lævorotatory, and acetic acid restores the rotatory power to its normal value.

Glutamine is completely precipitated by basic lead acetate only after remaining 8—10 hours. Since Schulze and Bosshard's glutamine was optically inactive (*Land. Ver. Stat.*, 29, 295), it would seem probable that optical isomerides may exist. E. W. W.

Decomposition of Lactose by Calcium Oxide. The Constitution of Parasaccharin. HEINRICH KILIANI and PETER LOEFFLER (*Ber.*, 1904, 37, 1196—1203).—Considerable quantities of parasaccharin, as well as isosaccharin and metasaccharin, are obtained from lactose when it is kept for some weeks in presence of calcium oxide. A modification of the former method of separation (compare Abstr., 1883, 565 and 962) is described. Parasaccharin, on oxidation with hydrogen peroxide and iron by Ruff and Fenton's method, yields *parasaccharopentose*, $C_5H_{10}O_4$, which crystallises in colourless prisms and plates, melts at $81.5-82^\circ$, and shows no optical activity. It forms a *phenylbenzylhydrazone* melting at $112-114^\circ$, and must have the following constitution: $OH \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH(OH) \cdot CH_2 \cdot OH$. The formula $OH \cdot CH_2 \cdot CH_2 \cdot C(OH)(CO_2H) \cdot CH(OH) \cdot CH_2 \cdot OH$ is therefore ascribed to parasaccharic acid.

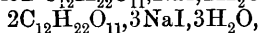
The various saccharic acids form crystalline quinine salts, which may be used for their identification.

Quinine metasaccharate crystallises in little nodules from ether, melting at $134-135^\circ$, and soluble in 9.6 parts of cold 50 per cent. alcohol.

Quinine parasaccharate also melts at $134-135^\circ$, but is soluble in 0.93 part of 50 per cent. alcohol.

Quinine saccharate melts at $141-142^\circ$, whilst *quinine isosaccharate* melts at $191-192^\circ$, and is only sparingly soluble in cold water and cold 50 per cent. alcohol. E. F. A.

Compounds of Sucrose with some Metallic Salts. D. GAUTHIER (*Compt. rend.*, 1904, 138, 638—639. Compare this vol., i, 144).—Sucrose forms a crystalline compound with sodium iodide which has the composition $C_{12}H_{22}O_{11} \cdot NaI \cdot 2H_2O$ and not



as stated by Gill (this Journal, 1871, 272). Ammonium, potassium, sodium, and barium thiocyanates also form compounds with sucrose which crystallise in beautiful, prismatic crystals, and are represented by the formulæ $C_{12}H_{22}O_{11} \cdot NH_4CNS \cdot 1.5H_2O$, $C_{12}H_{22}O_{11} \cdot KCNS \cdot H_2O$, $C_{12}H_{22}O_{11} \cdot NaCNS \cdot H_2O$, and $C_{12}H_{22}O_{11} \cdot Ba(CNS)_2 \cdot 2H_2O$ respectively.

M. A. W.

Hydrolysis of Maltose and of Dextrin by Dilute Acids and the Estimation of Starch. WILLIAM A. NOYES, GILBERT CRAWFORD, CHARLES H. JUMPER, EDGAR L. FLORY, and ROBERT B. ARNOLD (*J. Amer. Chem. Soc.*, 1904, 26, 266—280).—The hydrolysis of maltose and dextrin with hydrochloric acid proceeds at first approximately in accordance with the law of mass action, but afterwards becomes much

slower than would be expected. When maltose is heated with a 2.5 per cent. solution of hydrogen chloride, the maximum reducing power is attained in about an hour at 100° or in 20—30 minutes at 111°, and corresponds to a hydrolysis of 96—98 per cent. The reducing power of dextrose is not appreciably affected by this treatment. The hydrolysis of maltose is more complete in a solution of 2.4 per cent. strength than in one containing only 0.5 per cent. The rate of hydrolysis of dextrin with hydrochloric acid is only about one-half of that of maltose; after heating for an hour at 100°, 90 per cent. is hydrolysed, whilst after 2 hours the proportion hydrolysed is not quite 95 per cent.

When a solution of starch containing 0.5 per cent. is hydrolysed with extract of malt, the reducing power of the product after heating with hydrochloric acid indicates that it consists of 74—78 per cent. of maltose and 22—26 per cent. of dextrin. The hydrolysis of a solution of maize starch containing 0.5 per cent. with 2.5 per cent. hydrochloric acid amounts to 97 per cent. in an hour and 98 per cent. in 4 hours.

The following method is recommended for the estimation of starch. The starch is first converted into a mixture of maltose and dextrin by means of malt extract and, after filtration, 10 per cent. by volume of hydrochloric acid of sp. gr. 1.125 is added. The mixture is heated for an hour at 100°, and, when cold, a quantity of sodium hydroxide is added sufficient to neutralise 90 per cent. of the hydrochloric acid present; the solution is now made up to a definite volume, and the reducing power determined by means of Fehling's solution. One hundred parts of dextrose found in this manner correspond with 93 parts of starch in the original material.

E. G.

Coagulation of Starch. AUGUSTE FERNBACH and JULES WOLFF (*Ann. Inst. Pasteur*, 1904, 18, 165—180).—Malt extract contains a diastase (amylo-coagulase) which coagulates soluble starch. Coagulation was found to take place more readily at 8° than at 22°, whilst at higher temperatures, 26°, for example, no coagulation took place. The diastase is destroyed by heating for 5 minutes at 63°. Small amounts of soda were found to be favourable to coagulation, owing, perhaps, to its action on the amylase, which is more sensitive to soda than amylo-coagulase.

The coagulase was found to contain amylo-cellulose (Brown and Heron) in very variable amounts according to the conditions (temperature, time, &c.) under which it was produced (compare Maquenne, this vol., i, 17).

N. H. J. M.

Amylocellulose formed by the Action of Diastase. AUGUSTE FERNBACH and JULES WOLFF (*Compt. rend.*, 1904, 138, 819—821. Compare Abstr., 1903, i, 679; this vol., i, 17, 227, 228, 294).—The reversion of starch paste or its partial conversion into amylocellulose appears to be started initially by the action of diastase, and then to proceed spontaneously. Experiments made on the extent and rate of formation of amylocellulose in solutions of starch which had been heated to 120° showed that those solutions which had not been treated with malt extract, or those which had been treated with a small quantity of previously boiled malt extract, only contained traces of

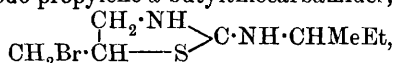
amylocellulose even when left for 24 hours; whilst solutions which had been sown with a small quantity of unboiled malt extract contained large quantities of amylocellulose after being left for 24 hours, even if the solution, 15 minutes after mixing, had been heated to a temperature much higher than that required to destroy the diastase in malt extract. M. A. W.

[Stability of Schönbein's Gun-cotton.] A Correction. FRITZ FICHTER (*Ber.*, 1904, 37, 1074—1076).—Contrary to the statement contained in Will's lecture on explosives (*ibid.*, 291), the gun-cotton cartridges prepared by Schönbein in 1846 and kept in the Bernoullianum at Basle, are still completely active; one was fired after 25 years, and another, by Prof. Piccard, after 50 years, in connection with the Schönbein festival in 1899. T. M. L.

Dextrorotatory *sec.*-Butylamine. JOHANNES GADAMER (*Arch. Pharm.*, 1904, 242, 48—51).—An introduction to the following paper. C. F. B.

Alkylated *d*-Butylthiocarbamides and -carbamides. W. URBAN (*Arch. Pharm.*, 1904, 242, 51—85).—Alkylated *d*-butylthiocarbamides were prepared by heating *d*-butylthiocarbimide, $\text{CS:N}\cdot\text{CHMeEt}$ (essential oil of *Cochlearia officinalis*; Gadamer, *Abstr.*, 1899, i, 534; 1901, i, 582), with amines of the type $\text{NH}_2\text{R}'$, NHR_2' , and NHR'' (including piperidine) in alcoholic solution. These thiocarbamides were converted into the corresponding carbamides, some (dissolved in slightly diluted alcohol) by digestion with moist yellow mercuric oxide at the ordinary temperature, others by warming a similar solution gently with silver nitrate, and nearly neutralising from time to time with barium hydroxide the nitric acid formed in the reaction.

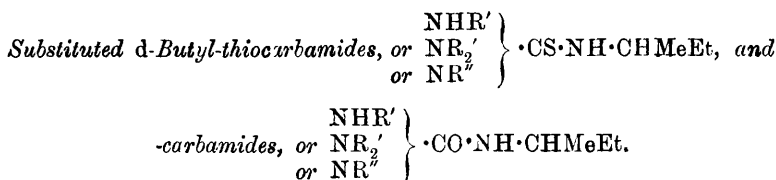
Bromo- and iodo-propylene-*d*-butylthiocarbamides,



&c., were prepared by mixing bromine or iodine with *d*-butylallylthiocarbamide, $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{CHMeEt}$, in ethereal solution, and decomposing with sodium hydroxide the hydrobromide, &c., that is formed. Chlorine, dissolved in carbon tetrachloride, seems to react in the same way as bromine and iodine, but a pure product could not be isolated.

Incidentally, *r*-*sec.*-butyloxamic acid, $\text{CO}_2\text{H}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHMeEt}$, melting at 88—89°, was prepared by heating with excess of oxalic acid at 180° the inactive *r*-*sec.*-butylamine obtained by reducing methyl-ethylketoxime with sodium amalgam.

The melting points (m. p.) of the substances prepared are recorded in the accompanying table, and also the molecular rotations $[\text{M}]$ (equal to $[\alpha] \times \text{mol. wt.}/100$) in alcoholic and in chloroform solutions. The rotation was measured at 20° with sodium light, and in solutions of *N*/8 strength, except in one or two cases, where weaker solutions had to be used. The substances are tabulated in order of increasing



| R', or R ₂ ', or R''. | M. p. | [M] _D ^{20°} in | | Mol. wt. | R. |
|--|-----------|------------------------------------|----------------------|----------|-------|
| | | Alcohol. | Chloro- form. | | |
| ¹ Hydrogen (<i>d</i> -butylcarbamide). | 166° | + 28·0° | ⁵ + 32·0° | 116·2 | 59·1 |
| „ (<i>d</i> -butylthiocarb- amide) | 137 | 29·2 | 32·9 | 132·2 | 75·2 |
| ² Ethyl | 92 | — | — | — | — |
| Methyl (thio)... | 84 | 44·6 | 43·2 | 146·3 | 89·2 |
| ² Propyl | 80 | 36·8 | 33·6 | 158·2 | 101·2 |
| ² <i>iso</i> Propyl | 134 | 34·4 | 33·2 | 158·2 | 101·2 |
| Ethyl (thio)... | 67 | 40·2 | 40·2 | 160·3 | 103·2 |
| Dimethyl (thio)... | 54 | 108·0 | 72·6 | 160·3 | 103·2 |
| ³ <i>n</i> -Butyl | 47 | 32·4 | 32·4 | 172·2 | 115·2 |
| ³ <i>r</i> -Butyl | 132 | 42·4 | 30·8 | 172·2 | 115·2 |
| <i>d</i> -Butyl | — | 71·2 | 67·6 | 172·2 | 115·2 |
| Allyl (thio)... | 31·5—32 | 36·2 | 35·0 | 172·3 | 115·2 |
| Propyl (thio)... | 53 | 40·6 | 41·4 | 174·3 | 117·2 |
| <i>iso</i> Propyl (thio)... | 112—112·5 | 36·8 | 34·6 | 174·3 | 117·2 |
| Diethyl (thio)... | 60—60·5 | 66·0 | 51·8 | 188·3 | 131·2 |
| <i>n</i> -Butyl (thio)... | 32 | 36·8 | 36·8 | 188·3 | 131·2 |
| <i>iso</i> Butyl (thio)... | 51 | 36·8 | 43·6 | 188·3 | 131·2 |
| <i>r</i> -Butyl (thio)... | 103 | 31·2 | 32·8 | 188·3 | 131·2 |
| <i>tert</i> -Butyl (thio)... | 132 | 28·8 | 35·6 | 188·3 | 131·2 |
| <i>d</i> -Butyl (thio)... | — | 73·6 | 69·2 | 188·3 | 131·2 |
| ² Phenyl | 150 | 46·4 | ⁴ 53·2 | 192·3 | 135·2 |
| Pentamethylene (thio)... | 114 | 128·4 | 78·8 | 200·3 | 143·2 |
| <i>iso</i> Amyl (thio)... | 43—44 | 42·4 | 40·4 | 202·2 | 145·1 |
| Phenyl (thio)... | 88 | 65·8 | 78·4 | 208·3 | 151·2 |
| Benzyl | 105 | 35·2 | 32·4 | 208·3 | 151·2 |
| Hexyl (thio) .. | oil | 32·0 | 31·2 | 216·3 | 159·2 |
| ³ Benzyl (thio)... | 58 | 43·6 | 38·0 | 222·3 | 167·2 |
| ³ <i>Diisobutyl</i> | 84 | 55·2 | 46·8 | 228·3 | 171·2 |
| <i>Diisobutyl</i> (thio)... | 33 | 68·8 | 49·6 | 244·3 | 187·2 |
| Tetrahydroquinolyl (thio)... | 40 | 128·0 | 89·6 | 248·3 | 191·2 |
| Tetrahydro <i>iso</i> quinolyl (thio)... | 117 | 99·2 | 66·4 | 248·3 | 191·2 |
| Bromopropylene | 92—93 | 55·6 | 52·4 | 251·2 | 194·1 |
| α -Naphthyl (thio)... | 135 | ⁴ 64·4 | 48·4 | 258·3 | 201·2 |
| β -Naphthyl (thio)... | 120 | 67·6 | 77·6 | 258·3 | 201·2 |
| <i>Diisomyl</i> (thio)... | oil | 84·8 | 60·8 | 272·4 | 215·3 |
| ³ Dibenzyl | 69 | 52·4 | 48·4 | 296·2 | 239·1 |
| Iodopropylene (thio)... | 114 | 59·2 | 54·0 | 298·1 | 241·0 |
| Dibenzyl (thio)... | 56 | 56·0 | 30·2 | 312·3 | 255·2 |

¹ From butylamine sulphate and potassium cyanate.² Prepared by means of mercuric oxide.³ Prepared by means of silver nitrate.⁴ In *N*/16 solution.⁵ In *N*/32 solution.

molecular weight; the weight of the fourth group, R, that is attached to the asymmetric carbon atom in addition to H, Me, and Et, is also tabulated.

Consideration of the table shows that the weight of this fourth group, R, has but little influence on the molecular rotation; also that the influence of the solvent is very marked. The introduction of a second alkyl group usually raises the molecular rotation, and more so in alcoholic than in chloroform solution. Among the butyl derivatives, the molecular rotation is greatest when the nitrogen atom is joined to CH_2 , less when to CH, and least when to C. In almost all cases the carbamide has a smaller molecular rotation than the corresponding thiocarbamide. Comparison of allyl- with propyl-*d*-butylthiocarbamide shows that the presence of a $\gamma:\delta$ double linking lowers the rotation. The existence of a nitrogen atom in a closed ring increases the rotation, usually to an amount greater than that due to the presence of a closed ring merely attached to the nitrogen atom. No regularity can be detected in the influence of homologous groups. The rotation caused when two asymmetric carbon atoms are present cannot be represented as the sum of two rotations each caused by one of these atoms.

C. F. B.

Amino-alcohols of the Type $\text{OH}\cdot\text{CMeR}\cdot\text{CH}_2\cdot\text{NMe}_2$. ERNEST FOURNEAU (*Compt. rend.*, 1904, 138, 766—768).—By the action of a secondary or tertiary amine on Tiffeneau's chlorohydrins, $\text{OH}\cdot\text{CMeR}\cdot\text{CH}_2\text{Cl}$ (compare Abstr., 1902, i, 449), a yield of 80 per cent. of the corresponding amino-derivative is obtained. These amino-alcohols boil without decomposition under the ordinary pressure; the lower members of the series are very soluble in water, and they are all more soluble in cold than in hot water, and reduce acidified solutions of permanganate only on warming. Their salts crystallise with difficulty, and the double salts are either very soluble, as the mercurichlorides or platinichlorides, or are easily decomposed, as the aurichlorides; the corresponding benzoyl derivatives, however, crystallise well, and serve to characterise the parent base. The salts all possess the characteristic physiological property of inducing local anæsthesia. *Dimethyl-amino-tert.-butyl alcohol*, $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{NMe}_2$, boils at 60° under 48 mm. pressure, the *benzoyl* derivative crystallises from alcohol in large efflorescent cubes which melt at 202° .

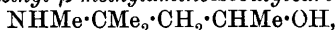
Methylethyl-dimethylaminomethylcarbinol boils at 57° under 23 mm. pressure; the *hydrochloride* of the *benzoyl* derivative crystallises from alcohol in brilliant, slender needles melting at 175° ; very soluble in water, methyl alcohol, or ethyl acetate; the *oxalate* melts at 145° .

Methylpropyl-dimethylaminomethylcarbinol boils at 78° under 35 mm. pressure; the corresponding *chlorohydrin* boils at 75° under 28 mm. The *hydrochloride* of the *benzoyl* derivative of the amino-alcohol, crystallises from a mixture of alcohol and ether in slender, hygroscopic needles which melt at 141° . The *chlorohydrin*, $\text{OH}\cdot\text{CMe}(\text{C}_5\text{H}_{11})\cdot\text{CH}_2\text{Cl}$, boils at 96° under 23 mm. pressure, and yields *methylisoamyl-dimethylaminomethylcarbinol*, which boils at 98° under 24 mm. pressure, is sparingly soluble in water, and has a strong odour; the *hydrochloride* of the *benzoyl* derivative crystallises from a mixture of alcohol and

ether in brilliant, silky needles melting at 138° and insoluble in acetone. *Phenylmethyldimethylaminomethylcarbinol*, $\text{OH}\cdot\text{CPhMe}\cdot\text{CH}_2\cdot\text{NMe}_2$, boils at about $135\text{--}136^{\circ}$ under 32 mm. pressure; the hydrochloride crystallises in spangles and melts at $159\text{--}160^{\circ}$; the hydrochloride of the benzoyl derivative crystallises from methyl alcohol in brilliant, flat crystals melting at $205\text{--}206^{\circ}$, and is sparingly soluble in alcohol or cold water.

The *chlorohydrin*, $\text{OH}\cdot\text{CMe}(\text{CH}_2\text{Ph})\cdot\text{CH}_2\text{Cl}$, boils at 155° under 25 mm. *Benzylmethyldimethylaminomethylcarbinol* boils at 144° under 24 mm.; the hydrochloride of the benzoyl derivative crystallises from alcohol in slender needles or from methyl alcohol in large, transparent, hard prisms which melt at 195° .
M. A. W.

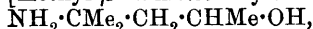
Derivatives of Diacetonalkamines. MORITZ KOHN (*Monatsh.*, 1904, 25, 135—148. Compare Abstr., 1902, i, 349, and this vol., i, 18).—Sodium amalgam reduces an acidified solution of methyldiacetonamine, prepared from mesityl oxide and methylamine, to *methyl-diacetonalkamine* [*methyl- β -methylaminoisobutylcarbinol*],



an oily liquid, with ammoniacal odour, boiling at $184.5\text{--}185.5^{\circ}$ (uncorr.). The *platinichloride*, $(\text{C}_7\text{H}_{17}\text{ON})_2\cdot\text{H}_2\text{PtCl}_6$, is a yellow, crystalline precipitate. Dimethyldiacetonamine is reduced in similar manner to *dimethyldiacetonalkamine* [*methyl- β -dimethylaminoisobutylcarbinol*], $\text{NMe}_2\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$, a limpid liquid with ammoniacal odour boiling at $186\text{--}190^{\circ}$. The *platinichloride*, $(\text{C}_8\text{H}_{19}\text{ON})_2\cdot\text{H}_2\text{PtCl}_6$, is an orange-red, crystalline powder.

An attempt was made to prepare these compounds by methylation of methyl- β -aminoisobutylcarbinol, but without success, an ammonium base being formed. The same base is obtained by methylation of methyl- or dimethyl-diacetonalkamines.

Diacetonalkamine [*methyl- β -aminoisobutylcarbinol*],



is best prepared by reduction of diacetonamine by sodium amalgam in hydrochloric acid solution (compare Kahan, Abstr., 1897, i, 494). Warming with methyl alcohol and methyl iodide converts it into a mixture of bases, consisting chiefly of methyldiacetonalkamine and a white solid. The latter compound is obtained in larger proportion when an excess of methyl iodide is employed. It is a methiodide containing admixed iodoform. When shaken with silver chloride, filtered, and precipitated by gold chloride, the *aurichloride*, $\text{C}_9\text{H}_{22}\text{ONAuCl}_4$, is obtained, crystallising from water in glistening, golden-yellow needles and melting at $157\text{--}159^{\circ}$. The *picrate*, $\text{C}_{15}\text{H}_{24}\text{O}_8\text{N}_4$, crystallises from alcohol in yellow leaflets and melts at $141\text{--}143^{\circ}$. The same product is obtained on methylating methyl- and dimethyl-diacetonalkamines; in the latter case, the *methiodide* was also isolated in the form of a white solid. The ammonium base formed must have the constitution $\text{OH}\cdot\text{NMe}_3\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$, and is a homologue of homocholine, $\text{OH}\cdot\text{NMe}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ (Schmidt and Partheil, Abstr., 1892, 950).
C. H. D.

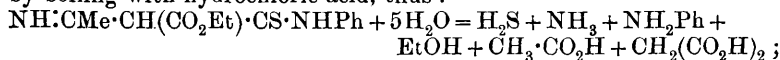
Preparation of Ethyl Chloroaminocrotonate. ADRIAAN LINDNER and ROBERT BEHREND (*Annalen*, 1903, 329, 367).—Ethyl chloro-

aminocrotonate (Abstr., 1900, i, 210; 1902, i, 14) can be most readily prepared in yields of 71—76 per cent. by shaking an ethereal solution of ethyl aminocrotonate, cooled with ice, with the calculated quantity of potassium hypochlorite for a quarter of an hour; the ethereal solution is dried with sodium sulphate and evaporated, and the residue crystallised from petroleum. The hypochlorite solution is prepared by saturating a 10 per cent. solution of potassium hydroxide with chlorine, when a 6—8 per cent. solution of hypochlorite is obtained, which should not be acid nor contain a great excess of alkali hydroxide.

K. J. P. O.

Condensation of Ethyl Aminocrotonate with Thiocarbimides.

ROBERT BEHREND and PAUL HESSE (*Annalen*, 1903, 329, 341—350).—It has been previously shown (Abstr., 1901, i, 136) that with ethyl aminocrotonate, phenylthiocarbimide forms an additive product, ethyl iminoacetylphenylthiomalonamate, and, further, that these two substances condense together with elimination of alcohol, forming thion-phenylmethyluracil. On treating the ester with silver carbonate in the presence of a small quantity of water, it is converted into ethyl iminoacetylmalonanilate, which melts at 125—126° and is identical in all respects with the substance directly prepared from phenylcarbimide and ethyl aminocrotonate (*loc. cit.*). The ester is completely hydrolysed by boiling with hydrochloric acid, thus:



at the same time, a trace of phenylthiocarbamide appears to be formed.

When methylthiocarbimide is used instead of phenylthiocarbimide, corresponding reactions take place; *ethyl iminoacetylmethylthiomalonamate*, $\text{NH}\cdot\text{CMe}\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{CS}\cdot\text{NHMe}$, is prepared by heating a mixture of mol. proportions of methylthiocarbimide and ethyl aminocrotonate at 100°, and extracting the product with ether to remove unchanged material and with sodium hydroxide to remove methylthionuracil; the substance crystallises in prisms or needles of a pale yellow colour melting at 145—146°. On treatment with silver carbonate, it loses sulphur and is converted into *ethyl iminoacetylmethylmalonamate*, $\text{NH}\cdot\text{CMe}\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{CO}\cdot\text{NHMe}$, which forms colourless crystals

melting at 124—126°. *Dimethylthionuracil*, $\text{NMe}\langle\begin{smallmatrix} \text{CO}\cdot\text{CH} \\ \text{CS}\cdot\text{NH} \end{smallmatrix}\rangle\text{CMe}$, is formed when the thiocarbimide and the ester are heated together at 150°, but only in a yield of 10 per cent.; it crystallises in white leaflets melting at 271—273°. The thionuracil is also produced when methylthiocarbimide and the ester are heated together at 100° with water, and when methylthiocarbamide is used instead of the carbimide. Ethyl acetoacetate and methylthiocarbamide do not yield the thionuracil.

On heating the dimethylthionuracil with concentrated hydrochloric acid under pressure at 160°, it is completely converted into 1:4-dimethyluracil (m. p. 261—262°; Behrend and Dietrich, 1900, i, 120).

K. J. P. O.

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Solubility of β -L-Asparagine and β -L-Aspartic Acid. HARRY W. BRESLER (*Zeit. physikal. Chem.*, 1904, 47, 611—617).—The solubility in each case increases as the temperature rises, as shown by determinations at various points between 0° and 100°. The variation of solubility with temperature is represented graphically and by formulæ.

J. C. P.

Alkyl Derivatives of Barbituric Acid. EMANUEL MERCK (D.R.-P. 146948, 146949, 147278, 147279, and 147280. Compare Abstr., 1903, i, 799).—The esters of dialkylmalonic acids condense with carbamide in presence of metallic ethoxides when the reacting compounds are heated together, alone or in alcoholic solution, forming CC-dialkylbarbituric acids. Alkali metals or their amides may be used in place of metallic ethoxides. The same derivatives are obtained from the acyl derivatives of carbamide, thus diethylbarbituric acid is obtained from ethyl diethylmalonate and acetylcarbamide or *propionylcarbamide*, the latter being prepared from propionyl chloride and carbamide, and melting at 209° (corr.).

Dimethylmalonic acid, carbamide, and phosphorus oxychloride form dimethylbarbituric acid, whilst the diethyl and higher derivatives form ureides of dialkylacetic acids (compare Abstr., 1903, i, 798). If, however, the dialkylmalonic acid is converted into the chloride by means of phosphorus chloride, the condensation with carbamide takes place readily: $\text{CR}_2(\text{COCl})_2 + \text{CO}(\text{NH}_2)_2 = \text{CR}_2 \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} \text{CO} + 2\text{HCl}$.

Esters of monoalkylmalonic acids also condense with carbamide in presence of alkali ethoxides. *Methylbarbituric acid*, $\text{C}_5\text{H}_6\text{O}_3\text{N}_2$, from diethyl methylmalonate, carbamide, and sodium ethoxide, crystallises from water in microscopic prisms or plates, and melts at 202—203° (corr.). The *sodium* salt, $\text{C}_{10}\text{H}_{11}\text{O}_6\text{N}_4\text{Na}$, crystallises in microscopic prisms containing water.

C. H. D.

[Preparation of Alkali Cyanides and Cyanamides.] DEUTSCHE GOLD- & SILBER-SCHNEIDE-ANSTALT VORM. RÖSSLER (D.R.-P. 148045 and 148046. Compare Abstr., 1902, i, 354).—Carbon reacts with sodamide or potassamide at 350—400°, forming the metallic derivative of cyanamide, $2\text{NaNH}_2 + \text{C} = \text{Na}_2\text{N}_2\text{C} + 2\text{H}_2$. Hydrocarbons, &c., may be employed in place of free carbon, or the alkali metal may first be fused, the requisite quantity of carbon then added, and ammonia passed into the mass, the temperature being maintained at first at 400°, and then, as the cyanamide is formed, gradually raised to 600°. On heating further to 800°, the reaction $\text{Na}_2\text{N}_2\text{C} + \text{C} = 2\text{NaCN}$ takes place. The sodium or potassium may also be employed in the form of an alloy with lead.

C. H. D.

Phosphorus-Nitrogen Bases of the Type $\text{P}(\text{NHR})_3\text{NR}$. PAUL LEMOULT (*Compt. rend.*, 1904, 138, 815—817. Compare Abstr., 1903, i, 672).—By the action of phosphorus pentachloride on *o*-toluidine or *as-m*-xylylidine ($\text{NH}_2 : \text{Me} : \text{Me} = 1 : 2 : 4$), the homologues of trianilino-phenylphosphimide in the form of their hydrochlorides are obtained,

together with the corresponding arylamide of orthophosphoric acid, $\text{PO}(\text{NHR})_3$; the two are readily separated by the difference of their solubility in alcohol. The bases are much less stable than the corresponding aniline base, and have not been obtained in a free state, but the following salts are described: (1) from *o*-toluidine, the hydrochloride, $\text{P}(\text{NH}\cdot\text{C}_7\text{H}_7)_4\text{Cl}$, already described by Gilpin (compare Abstr., 1897, i, 463) can be obtained in beautiful needles 2—3 mm. long from concentrated hot alcoholic solution, which are active towards polarised light, melt and decompose at 254° , and are decomposed by alcoholic sodium hydroxide or sodium ethoxide, yielding *o*-toluidine; the *nitrate*, $\text{P}(\text{NH}\cdot\text{C}_7\text{H}_7)_4\cdot\text{NO}_3$, obtained by the action of alcoholic silver nitrate on the preceding salt, crystallises in beautiful, white, silky needles, melting at 250° and deflagrating at a higher temperature; the *platinichloride*, $[\text{P}(\text{NH}\cdot\text{C}_7\text{H}_7)_4\text{Cl}]_2\cdot\text{PtCl}_4$, forms dull yellowish-red crystals, which are decomposed on boiling with alcohol, and blacken and decompose at $235\text{--}240^\circ$. (2) From *as-m*-xylylidine, the *chloride*, $\text{PCl}(\text{NH}\cdot\text{C}_8\text{H}_9)_4$, crystallises from alcohol, melts and decomposes at 264° , and is decomposed by alcoholic alkali hydroxides yielding *as-m*-xylylidine; the *nitrate*, $\text{P}(\text{NH}\cdot\text{C}_8\text{H}_9)_4\cdot\text{NO}_3$, obtained by double decomposition, melts and decomposes at $246\text{--}248^\circ$, and crystallises in beautiful, silky needles; the *platinichloride*, $[\text{P}(\text{NH}\cdot\text{C}_8\text{H}_9)_4\text{Cl}]_2\cdot\text{PtCl}_4$, forms a pale red, sandy, crystalline precipitate which decomposes at 260° .

M. A. W.

Amphoteric Electrolytes, especially Cacodylic Acid. ARTHUR HANTZSCH (*Ber.*, 1904, 37, 1076—1084).—Zawidzki (Abstr., 1903, i, 801) has suggested that cacodylic acid acts as a pseudo-acid, because whilst its affinity constant is only $k=4\cdot2\times 10^{-7}$, as compared with $3\cdot0\times 10^{-7}$ for carbonic acid, it still forms a neutral sodium salt, and he has further suggested as an alternative view that ‘amphoteric electrolytes’ behave in this way, and may yield neutral salts with bases, in spite of having exceedingly slight acid properties. That Zawidzki’s conclusions are based on an incorrect interpretation of the experimental evidence is shown by the following considerations. There is nothing abnormal in the fact that cacodylic acid can be sharply titrated by using phenolphthalein as indicator, for it yields only a monobasic salt under these conditions, and carbonic acid can be equally sharply titrated; this was tested by preparing dilute aqueous solutions of carbonic acid by mixing an aqueous carbonate with the calculated quantity of acid, and titrating the carbonic acid by means of sodium hydroxide; the quantity of sodium hydroxide used exactly corresponded with the amount required to produce the salt NaHCO_3 . Again, it can be calculated from the dissociation constant of cacodylic acid ($k=4200\times 10^{-10}$) that the sodium salt should be hydrolysed in *N*/40 solution to the extent of 0·11 per cent.; the actual values, 0·097, 0·093, 0·095, 0·096, 0·099, determined from experiments on the hydrolysis of ethyl acetate, are perfectly normal, and give no indication that cacodylic acid is anything but a simple weak monobasic acid.

That cacodylic acid has an exceedingly slight tendency to act as a dibasic acid is shown by the fact that on mixing sodium cacodylate

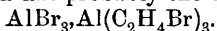
and sodium hydroxide in $N/9.6$ solution at 25° the electrical conductivity is 25 units (10 per cent.) less than that calculated from a simple additive law, whilst in the case of sodium chloride the decrease is only 12.4 units, and in the case of sodium acetate 15.2 units; the effect is, however, very slight and entirely disappears in $N/48$ solution.

The view that cacodylic acid is an amphoteric electrolyte is based on the fact that it yields a chloride and a nitrate. It is pointed out, however, that these are not derived from cacodylic acid, but from the hydrate, and have the formulæ $\text{AsMe}_2(\text{OH})_2\text{Cl}$ and $\text{AsMe}_2(\text{OH})_2\cdot\text{NO}_3$, and not $\text{AsMe}_2\text{O}\cdot\text{Cl}$ and $\text{AsMe}_2\text{O}\cdot\text{NO}_3$, as should be the case if they were derived from an amphoteric cacodylic acid. Again, cacodylic acid, presumably in the form of the hydrate $\text{AsMe}_2(\text{OH})_3$, from which the acid salts are derived, has a basic dissociation-constant, 4.05×10^{-13} , and should be a stronger base than dimethylpyrone ($K = 2.7 \times 10^{-13}$); this is shown to be the case by the fact that its hydrochloride is less dissociated and has a lower conductivity.

The author concludes that in aqueous solution there is an equilibrium between cacodylic acid, which is ionised as an acid and yields metallic salts, $\text{AsMe}_2\text{O}\cdot\text{O}^-\text{H}^+ \rightarrow \text{AsMe}_2\text{O}\cdot\text{O}^-\text{Na}^+$, and its hydrate, 'cacodyl base' or 'cacodyl alcohol,' which is ionised as a base and yields salts with acids, $\text{AsMe}_2(\text{OH})_2/\text{OH}^- \rightarrow \text{AsMe}_2(\text{OH})_2^+\text{Cl}^-$.

T. M. L.

Catalytic Preparation of Organic Aluminium Compounds. J. A. FÜRSTENHOFF (*Chem. Centr.*, 1904, i, 785—786; from *Bull. Assoc. Belge Chim.*, 17, 414—426).—Aluminium does not act on cold ethylene dibromide, but at a temperature near the boiling point of the latter a compound is formed which has probably the composition



When a few drops of this compound are added to a mixture of aluminium and ethylene dibromide, the action takes place at the ordinary temperature, and in a similar manner aluminium acts on ethyl bromide in presence of this compound. The aluminium bromoalkyl compounds fume in the air, ultimately taking fire and forming dense acid fumes. Gustavson has prepared similar substances, but at higher temperatures, and they are probably, therefore, decomposition products of aluminium bromoalkyl compounds.

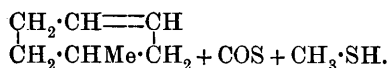
E. W. W.

Quadrivalent Oxygen. JULIUS VON BRAUN (*Chem. Centr.*, 1904, i, 867—868; from *Nachr. k. Ges. Wiss. Göttingen*, 1903, 331—335).—Acid amides react energetically with halogen alkyls in the presence of zinc or magnesium or with magnesium halogen alkyloxides; in some cases, the heat developed is sufficient to char the whole mass. The violence of the action may be moderated by dilution with benzene or ether. The products obtained resemble those prepared by the action of zinc and halogen alkyls on ketones or aldehydes; they are in most cases amorphous, gummy substances, and are readily soluble in benzene, but only slightly so in ether or light petroleum. These compounds contain carbon, nitrogen, metal, and halogen, and are

probably formed by the action of molecular proportions of amide and metal. They may be hydrolysed, but not so readily as magnesium halogen alkyl oxides, and then form the original acid amide and the hydrocarbon corresponding with the halogen alkyl used in their preparation. By the action of dilute sulphuric acid on the products prepared by the action of zinc and methyl iodide or propyl iodide respectively on diethylacetamide or dipropylacetamide, a 95 per cent. yield of the original amide and methane or propane is obtained. This reaction indicates a constitution of the type $\text{RN}_2 > \text{C} : \text{O} < \begin{smallmatrix} \text{R} \\ \text{MeCl} \end{smallmatrix}$. E. W. W.

Structure of Heptanaphthylenes and some of their Compounds. WLADIMIR B. MARKOWNIKOFF (*J. Russ. Phys. Chem.*, 1903, 35, 1049—1072).—The oxidation of the heptanaphthylene, prepared by the action of alcoholic potassium hydroxide on heptanaphthylene hydrobromide, by means of concentrated nitric acid yields mainly β -methyladipic acid, together with a small quantity of α -methyladipic acid. The heptanaphthylene therefore consists of a mixture of two constituents, the principal one having the double linking in the 3:4-position, and the other in the 2:3-position, the methyl group being in the 1-position.

The heptanaphthylene obtained from the xanthic ester, when oxidised with permanganate, yields succinic and oxalic acids, and must hence have the 3:4-structure. Its formation takes place according to the following equation:

$$\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 - \text{CH} \cdot \text{O} \cdot \text{CS}_2 \text{Me} \\ \text{CH}_2 \cdot \text{CHMe} \cdot \text{CH}_2 \end{array} =$$


The action of aqueous sulphuric acid (1 vol. acid to 1 of water) on 3:4-methylnaphthylene converts it partly into the 2:3- and 1:2-isomerides and partly into ordinary 3-methylhexanol ($\text{Me} : \text{OH} = 1 : 3$), the inactive stereoisomeride of the latter and 2-methylhexanol.

When treated with sulphuric acid diluted with half its volume of water, 3:4-heptanaphthylene undergoes polymerisation, yielding: (1) diheptanaphthylene, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 - \text{CH} - \text{C} = \text{CH} \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CHMe} \cdot \text{CH}_2 \quad \text{CH}_2 \cdot \text{CHMe} \cdot \text{CH}_2 \end{array}$, which is a viscous, colourless liquid having the sp. gr. 0.9128 at $0^\circ/0^\circ$ and 0.9119 at $20^\circ/0^\circ$; and $\alpha_D + 0.28^\circ$ in a 5 cm. tube. It instantly decolorises bromine, but not permanganate, whether in the pure state or in solution; with the former, it gives a dibromide, $\text{C}_{14}\text{H}_{24}\text{Br}_2$, and a dibromide of its monobromo-derivative, $\text{C}_{14}\text{H}_{23}\text{Br}_3$.

From these results and others previously obtained, the author draws the following conclusion. In the most simple form of six-membered cyclic hydrocarbon containing one substituted radicle, the influence of the latter is such that both in the splitting-off of hydrogen, together with a halogen or other group, and in the combination with a molecule containing mobile hydrogen, the latter splits off from, or combines preferably with, the carbon atom furthest removed from the side-chain, whilst the electro-negative element combines with the carbon nearest the side-chain.

T. H. P.

Cyclic Compounds. Heptanaphthylenes or Methylcyclohexenes. WLADIMIR B. MARKOWNIKOFF (*J. Russ Phys. Chem. Soc.*, 1904, **36**, 39—62).—After referring to the work of other authors on the heptanaphthylenes, the author gives the properties of 1-methyl- $\Delta^{3,4}$ -cyclohexene (see Markownikoff and Stadnikoff, *Abstr.*, 1903, i, 803) and some of its derivatives.

The *dibromide*, $C_7H_{12}Br_2$, is a colourless oil boiling at 130° under 40 mm. pressure; it has a strong camphor-like odour, and it gradually decomposes at the ordinary temperature; it has a sp. gr. 1.650 at $15^\circ/15^\circ$, and 1.648 at $20^\circ/15^\circ$, and $[\alpha]_D$ 9.01° at 20° . The *nitrosochloride*, $C_7H_{12}ONCl$, is a stable, heavy liquid with a pungent odour and a bright bluish-green colour; with alcoholic potassium hydroxide, it gives the original 1-methyl- $\Delta^{3,4}$ -cyclohexene. The iodide of the latter yields, with silver acetate, an inactive stereoisomeric *methylcyclohexene* which boils at 103.5° under 767 mm. pressure and has the sp. gr. 0.8172 at $0^\circ/0^\circ$, 0.7999 at $20^\circ/0^\circ$, and 0.80305 at $20^\circ/15^\circ$.

1-Methyl- $\Delta^{2,3}$ -cyclohexene was not obtained quite free from the $\Delta^{3,4}$ -isomeride; it has a lower specific rotation than the latter, and boils at about 105° under 760 mm. pressure.

1-Methyl- $\Delta^{1,2}$ -cyclohexene, $CMe \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH} - \text{CH}_2 \end{array} > CH_2$, is an optically inactive liquid with an odour resembling that of turpentine; it boils at $106\text{--}108^\circ$ (mainly at 107.5°) under 750 mm. pressure and at $108\text{--}110^\circ$ (mainly at 109°) under 768 mm. pressure; it has the sp. gr. 0.81658 at $0^\circ/0^\circ$, 0.80054 at $20^\circ/0^\circ$, and 0.80167 at $20^\circ/20^\circ$, its coefficient of expansion from 0° to 20° being 0.00082; it oxidises in the air even more rapidly than the $\Delta^{3,4}$ -isomeride. If a drop of the hydrocarbon is mixed with 10 c.c. of alcohol and sulphuric acid then carefully added, the surface of separation of the two layers becomes coloured bright yellow, which quickly changes to orange, while the upper alcoholic liquid turns blue; on shaking, the whole of the liquid assumes a bright green colour with a blue tint.

The work of Morris (*Trans.*, 1882, 167), Rénard (*Abstr.*, 1887, 565), and Maquenne (*Abstr.*, 1889, 32 and 361; 1892, 1065) is discussed.

T. H. P.

Friedel and Crafts' Reaction. IV. JACOB BOESEKEN (*Rec. trav. chim.*, 1904, **23**, 98—109. Compare *Abstr.*, 1900, i, 349; 1901, i, 474; 1903, i, 617 and 626).—The resinous substance, C_7H_6 , produced by the interaction of aluminium chloride with benzyl chloride may be composed of a ring of n groups of the type $C_6H_4 \cdot CH_2$ or $C_6H_5 \cdot CH$; the latter is the more probable, since a similar resinous product is obtained from either *p*-chloro- or *p*-bromo-benzyl chloride, whereas if the union were effected through the benzene ring, as a structure of the first type would imply, the introduction of a haloid atom in the *para*-position should inhibit, or at least diminish, the formation of resinous products. The production of the latter appears to depend on the simultaneous occurrence of hydrogen and chlorine atoms in the side-chain, since they are not formed when aluminium chloride reacts with diphenylmethane, diphenyldichloromethane, or triphenylmethane. In

this connection, the instability of *isobutyl* chloride and of diphenylchloromethane towards aluminium chloride is of interest (Abstr., 1903, i, 617).

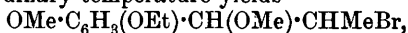
p-Nitrobenzyl chloride behaves differently (compare Perrier, Abstr., 1895, i, 510), forming with aluminium chloride an additive *product* (yellow spangles, stable at 100°) which reacts with benzene and its homologues at 50°, furnishing the corresponding *p*-nitrodiphenylmethanes. This additive product appears to be partially dissociated when dissolved in benzene, and it is perhaps the aluminium chloride so liberated which brings about the catalytic action. The author now regards the formation of such additive products as of secondary importance in the aluminium chloride condensation; they merely serve to increase the yield by preventing the destructive action of the condensing agent on the product formed. He also does not accept Kronberg's view as to the constitution of the additive compound of benzoyl chloride (Abstr., 1900, i, 502) with aluminium chloride, but prefers the formula $C_6H_5 \cdot CCl : O \begin{smallmatrix} \text{Cl} \\ \diagup \\ AlCl_3 \end{smallmatrix}$.

In the condensation of acyl chlorides with aromatic hydrocarbons or their derivatives, para-substituted ketones are almost invariably produced. This appears to be due to the directive influence of the aluminium chloride, which, it is suggested, is unable to form additive compounds of the type $C_6H_5 \cdot CO(AlCl_3) \cdot C_6H_4X$ with the substituent X in the ortho-position to the carbonyl. In the compounds of aluminium chloride with *p*-nitrodiphenylmethane and its derivatives, combination occurs at a different part of the molecule, and consequently this directive influence is no longer exerted. When *p*-nitrobenzyl chloride is condensed with benzene, *p*-nitrodiphenylmethane alone is formed, but with toluene an oily mixture of isomerides is produced, and with chlorobenzene a mixture of *p*-chloro-*p*-nitrodiphenylmethane (melting at 104°) and *o*-chloro-*p*-nitrodiphenylmethane (?), large crystals, melting at 67°. The corresponding bromo-derivatives are similarly obtained from bromobenzene; *o*-bromo-*p*-nitrodiphenylmethane (?) crystallises in long needles and melts at 73°. T. A. H.

Aromatic Propylene Compounds. IV. *iso*Eugenol Ethyl Ether. CARL HELL and HERMANN BAUER (*Ber.*, 1904, 37, 1128—1132. Compare Abstr., 1896, i, 20; 1903, i, 242, 479; this vol., i, 241; also Zincke, this vol., i, 41).—Aromatic propylene dibromides are divided into three groups. (1) Stable dibromides such as the dibromides of phenylpropylene and of *o*-anethole. These may in certain cases be distilled without decomposition, and are not acted on by water or alcohol. (2) Dibromides so unstable that they cannot be isolated, but immediately lose hydrogen bromide and yield bromopropylene compounds, for example, the dibromides of diphenylpropylene, phenylmethylpropylene, and phenylanisylpropylene. (3) Dibromides which are moderately stable, and which slowly react with water or alcohol, for example, the dibromides of *isoeugenol* ethers and of anethole.

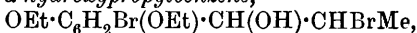
*iso*Eugenol ethyl ether dibromide when treated with aqueous acetone at 40° loses hydrogen bromide (2 mols.), and with methyl

alcohol at the ordinary temperature yields



melting at 69—70°.

Bromoethyleugenole, on treatment with alcoholic potash, is converted into the corresponding isoeugenole derivative, which readily forms an oily dibromide. With water, this dibromide yields 2-bromo-3-methoxy-4-ethoxy-1- β -bromo- α -hydroxypropylbenzene,



melting at 106—107°. The corresponding methyl ether melts at 63—64°. Dibromoethyl isoeugenole, $\text{OMe} \cdot \text{C}_6\text{HBr}_2(\text{OEt}) \cdot \text{CH} \cdot \text{CHMe}$, obtained from dibromoethyleugenole (Abstr., 1895, i, 656), crystallises in long, pale rose-coloured needles melting at 79.5°, and yields a dibromide, which melts at 70—71°. With warm water, the dibromide is slowly decomposed, yielding 2:5-dibromo-3-methoxy-4-ethoxy-1- α -hydroxy- β -bromopropyl benzene, $\text{OMe} \cdot \text{C}_6\text{HBr}_2(\text{OEt}) \cdot \text{CH}(\text{OH}) \cdot \text{CHBrMe}$, melting at 102—103°. The corresponding methyl ether melts at 63—64°.

J. J. S.

Ozonides of Simple Unsaturated Hydrocarbons. CARL D. HARRIES and ALFRED S. DE OSA (*Ber.*, 1904, 37, 842—845).—The product of the distillation of γ -amino- α -phenylbutane phosphate (Abstr., 1903, i, 815) is a mixture of α -phenyl- Δ^α -butylene and α -phenyl- Δ^β -butylene. Klages' method (Abstr., 1902, i, 669) yields pure α -phenyl- Δ^β -butylene, which does not form a nitrosite.

α -Phenyl- Δ^β -butylene ozonide, $\text{C}_{10}\text{H}_{12}\text{O}_3$, prepared by the action of ozone at a low temperature in complete absence of water, is a viscid, colourless, pungent-smelling syrup, exploding when heated on platinum foil, insoluble in water, but dissolving, probably with decomposition, in ether and alcohol. When distilled under 12 mm. pressure, a mobile liquid passes over, which has, however, the same composition, and the molecular weight of which corresponds with the formula $\text{C}_{10}\text{H}_{12}\text{O}_3$.

α -Phenyl- γ -methyl- Δ^β -butylene ozonide, $\text{CH}_2\text{Ph} \cdot \text{CH} \begin{smallmatrix} \diagup \text{CMe}_2 \\ | \\ \text{O}_3 \end{smallmatrix}$, is also a colourless, viscous oil.

In the action of ozone on phenylbutylene in presence of water, phenylacetaldehyde is produced, and not hydrocinnamaldehyde, as formerly stated.

C. H. D.

isoAmenylbenzene and toluene. FRANZ KUNCKELL and KARL ARTHUR STAHEL (*Ber.*, 1904, 37, 1087—1090).—A method is described by which isoamenylbenzene can be prepared with greater readiness than when using the method described by Schramm (Dafert, Abstr., 1883, 1094).

Phenyl α -bromoisobutyl ketone, $\text{COPh} \cdot \text{CHBr} \cdot \text{CHMe}_2$, prepared by the action of aluminium chloride on a solution of α -bromoisovaleryl bromide and benzene in carbon disulphide, crystallises from alcohol in colourless flakes and melts at 47°.

α -Chloro- β -bromoisamenylbenzene, $\text{CPhCl} \cdot \text{CBr} \cdot \text{CHMe}_2$, prepared by the action of phosphorus pentachloride on the preceding compound, is a colourless oil, which boils at 125—129° under 10 mm. pressure, decomposes when distilled under atmospheric pressure, and has a sp. gr.

1.28 at 15°; it is reduced by metallic sodium in ethereal solution to isoamenylnbenzene.

p-Tolyl α -bromoisobutyl ketone, $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CHBr} \cdot \text{CHMe}_2$, crystallises from alcohol in flakes and melts at 57°.

α -Chloro- β -bromoisamenylnbenzene, $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CCl} \cdot \text{CHBr} \cdot \text{CHMe}_2$, is an oil which boils at 130—140° under 16 mm. pressure, becomes green when kept, and has a sp. gr. 1.303 at 18°.

p-isoAmenylnbenzene, $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CH} \cdot \text{CHMe}_2$, is a colourless, aromatic oil, which boils at 106—107° under 10—11 mm. pressure, and has a sp. gr. 0.885 at 18°/4°, and n_D 1.5316 at 20°.

$\alpha\beta$ -Dibromoisamenylnbenzene, $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CHBr} \cdot \text{CHBr} \cdot \text{CHMe}_2$, crystallises from alcohol in colourless flakes and melts at 85°. The corresponding *di*-iodide crystallises from alcohol in pearly flakes and melts at 106—107°.

The boiling point of 1:2-dimethyl-4-allylbenzene is 110—112° under 16 mm. pressure, and not 165—168° as previously stated (Abstr., 1903, i, 617).
T. M. L.

Aromatic Nitro-compounds. XVII. Comparative Study of the Three Dinitrobenzenes. IV. Action of Potassium Cyanide. CORNELIS A. LOBRY DE BRUYN and J. W. VAN GEUNS (*Rec. trav. chim.*, 1904, 23, 26—38. Compare Abstr., 1885, 656, 657; 1891, 429; 1894, 573; 1899, i, 744, 745; and 1901, i, 460).—When a mixture of dry potassium cyanide and dinitrobenzene is heated, gas begins to be evolved at 160°, and if the temperature is very slowly raised to 210° the principal product is 2:2'-dinitrodiphenyl ether (Haeussermann and Bauer, Abstr., 1896, i, 676).

When an aqueous solution of potassium cyanide is employed, small quantities of *o*-nitrophenol and potassium cyanate and nitrite are produced, but most of the dinitrobenzene is recovered unchanged.

m-Dinitrobenzene begins to react with dry potassium cyanide at 160°, but as the temperature is raised to 235° complete decomposition ensues. With an aqueous solution of potassium cyanide, brown, humus-like decomposition products are formed.

p-Dinitrobenzene, when heated at 200—208° with dry potassium cyanide, gives off a gas having the percentage composition: nitric oxide 35, carbon dioxide 28, nitrogen 41. The principal product of the reaction is the di-*p*-nitrophenyl ether, described by Haeussermann and Teichmann (Abstr., 1896, i, 533). With an aqueous solution of potassium cyanide, ammonium carbonate and hydrocyanic acid are formed in addition to *p*-nitrophenol and 4:4'-dinitroazobenzene and 4:4'-dinitroazoxybenzene (Abstr., 1900, i, 194), the last mentioned being the principal product.

The interactions of the three dinitrobenzenes with potassium cyanide dissolved in alcohol have already been described (Abstr., 1885, 656 and 657). The authors are unable to confirm the observation of Hodgkinson and Hope (*Chemical News*, 1899, 20), that by the action of *m*-dinitrobenzene on dry potassium cyanide in dry alcohol, nitrobenzonitrile and not ethoxynitrobenzonitrile is produced; they find, however, that the presence of some water in the alcohol is essential to the formation of the latter,

Propoxy-nitrobenzonitrile, $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{OPr}^a) \cdot \text{CN}$ [$\text{CN} : \text{NO}_2 : \text{OPr}^a = 1 : 2 : 6$], produced in small amount by the action of potassium cyanide on *m*-dinitrobenzene dissolved in propyl alcohol, crystallises in slightly yellow, lustrous spangles, melts at 105° , and resembles its lower homologues in properties.

When *p*-dinitrobenzene is treated with potassium cyanide dissolved in methyl alcohol, *p*-nitroanisole is produced; with ethyl alcohol as a solvent, *p*-nitrophenetole is obtained. In both cases some 4 : 4'-dinitroazobenzene is also formed.

T. A. H.

Aromatic Nitro-compounds. XVIII. Comparative Study of the Three Dinitrobenzenes. V. Summary of Results. CORNELIS A. LOBRY DE BRUYN (*Rec. trav. chim.*, 1904, 23, 39—46).—A summary of the results of work already published by the author and collaborators (Abstr., 1885, 656, 657; 1891, 428; 1892, 305; 1894, 573; 1895, i, 654; 1899, i, 744, 745; 1900, i, 460, 461, 462, and preceding abstract).

The results show that the three dinitrobenzenes behave similarly towards hydrochloric acid and the halogens, the nitro-groups being wholly replaced in the ortho-compound and partially in the meta- and para-isomerides (only one nitro-group is replaced in the latter). In all other reactions, well-marked differences in behaviour are shown between the ortho- and meta-isomerides, and frequently also between the meta- and para-compounds. Examples of these differences are quoted from the previous papers.

T. A. H.

Aromatic Nitro-compounds. XIX. Action of Potassium Cyanide. CORNELIS A. LOBRY DE BRUYN (*Rec. trav. chim.*, 1904, 23, 47—61).—The changes induced by the action of potassium cyanide on aromatic nitro-compounds may be conveniently classified into three groups.

(1) *The reduction of the nitro-compounds, especially to azo-, azoxy-, and nitroso-derivatives or to amino- or hydroxy-compounds with the formation of potassium cyanate.*—Examples of such reactions are (a) the conversion of *o*-nitrobenzaldehyde into *o*-azoxybenzoic acid (Homolka, Abstr., 1884, 1342), in which case it is suggested that the aldehyde is first changed into *o*-nitrosobenzoic acid under the influence of light, and this is then reduced by the cyanide; (b) the action of potassium cyanide on dinitrophenols (Nietzki and Petri, Abstr., 1900, i, 485; Borsche, *ibid.*, 645; and with Locatelli, 1902, i, 226), and (c) the action of potassium cyanide on dinitrobenzenes (Lobry de Bruyn and Van Geuns, preceding page).

(2) *The replacement of the nitro-group by alkoxy-groups when the cyanide is used in alcoholic solution.*—Examples of this reaction are the formation of dinitroanisole from 1 : 2 : 4-trinitrobenzene and of alkoxy-nitrobenzonitriles from *m*-dinitrobenzene by the action of potassium cyanide dissolved in alcohols (Abstr., 1885, 657).

(3) *The introduction of cyano-groups either (a) by replacement of a nitro-group or (b) by indirect substitution of a hydrogen atom adjacent to a nitro-group.*—An example of the first type has recently been observed by Van Geuns in the author's laboratory, namely, the con-

version of alkoxydinitrobenzonitriles into dicyano-derivatives by the action of potassium cyanide dissolved in alcohols; this reaction appears to require the presence of a very mobile nitro-group. Examples of the second type of reaction are the conversion of para- and meta-halogenated nitrobenzenes into meta- and ortho-halogenated benzoic acids respectively, the formation of *o*-alkoxy nitrobenzonitriles from *m*-dinitrobenzene (Abstr., 1885, 656), the production of chloronitro-cyanoethoxybenzene from 1-chloro-2:4-dinitrobenzene (Van Heteren, Abstr., 1901, i, 460), and the formation of the purpuric acids from nitrophenols. The author agrees with Borsche that *isopurpuric* acid may contain the group $\text{NH}\cdot\text{OH}$, but suggests that there is also present a nitro- and a nitroso-group.

The formation of 2:6-dinitro-3-aminophenol from 2:4-dinitroaniline (Lippmann and Fleissner, Abstr., 1886, 791) by the action of potassium cyanide is explained by assuming that 2:6-dinitro-3-aminobenzonitrile is first formed, the cyanogen group being eventually replaced by a hydroxyl group.

It is suggested that the first step in these reactions is the assumption of a molecule of potassium cyanide by a nitro-group with the formation of a compound of the nitro-acid type (Hantzsch and Kissel, Abstr., 1900, i, 89), in which the cyanogen radicle is joined to the nitrogen atom. Such a compound naturally lends itself to intramolecular transposition, the cyanogen group passing to a neighbouring ortho-position, the residual nitro-group being disposed of in the various ways mentioned in the examples already quoted. These reactions do not take place unless there are replaceable hydrogen atoms in the ortho-positions to the nitro-group, and unless there is at least one other negative group (a nitro-group or a haloid atom; a hydroxyl group is insufficient) attached to the nucleus.

T. A. H.

Condensation of Aromatic Nitro-compounds with Compounds containing Reactive Methylene Groups. ARNOLD REISSERT (*Ber.*, 1901, 37, 831—838).—The addition of certain aldehydes and ketones, or of ethyl malonate, ethyl cyanoacetate, &c., to aromatic nitro-compounds in presence of aqueous or alcoholic alkali hydroxides produces intense blue or violet colorations, passing rapidly into red or brown. Acids precipitate brown condensation-products, which, however, prove to be uncrystallisable.

Nitrobenzene, acetone, and sodium methoxide react together vigorously on warming. After removal of aniline and azobenzene by distillation with steam and filtration from tarry products, hydrochloric acid precipitates a brown acid substance, and a second, lighter coloured compound, separates from the filtrate on cooling. Bromine water precipitates tribromoanilinoacetic acid from the solution.

m-Dinitrobenzene, acetone, and sodium ethoxide yield a brown acid compound according to the equation $\text{C}_6\text{H}_4(\text{NO}_2)_2 + \text{CH}_3\cdot\text{CO}\cdot\text{CH}_3 = \text{C}_9\text{H}_6\text{O}_5\text{N}_2 + 2\text{H}_2\text{O}$. An analysis of the barium salt, however, shows that the formula of the acid is probably $(\text{C}_9\text{H}_6\text{O}_5\text{N}_2)_5$.

1:5- and 1:8-Dinitronaphthalenes form similar compounds. 2:4-Dinitrophenol and acetone form a red, crystalline sodium salt, yielding a very unstable, violet solution on addition of acetic acid. *m*-Dinitro-

benzene and benzyl cyanide react in presence of sodium ethoxide according to the equation $2C_6H_4O_4N_2 + 2C_8H_7N = C_{28}H_{20}O_7N_6 + H_2O$. The reddish-brown acid sinters at 50° and decomposes at about 97° , and dissolves readily in alcohol, acetic acid, or chloroform, sparingly in water.

C. H. D.

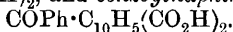
Preparation of Chlorinated Toluene-*o*-sulphonic Acids. FARBERWERKE VORM MEISTER, LUCIUS, & BRÜNING (D.R.-P. 146946).—Chlorine reacts with aqueous solutions of sodium toluene-*o*-sulphonate and its derivatives, causing substitution in the benzene ring. The sulpho-group is not eliminated, as is the case with benzenesulphonic acids. Thus chlorine precipitates a mixture of sodium *o*- and *p*-chlorotoluene-*o*-sulphonates from a cold solution of sodium toluene-*o*-sulphonate. The two acids are separated by fractional crystallisation of their aniline salts. The *p*-salt is the more sparingly soluble, and forms flat needles melting above 260° ; the *o*-salt is more readily soluble, and forms long needles melting at 249° . The action of chlorine on sodium toluene-*o*-sulphonate at 100° produces a mixture of 2:4-, 2:5-, and 3:4-dichlorotoluene-*o*-sulphonic acids. Sodium *o*-chlorotoluene-*o*-sulphonate and chlorine at 100° form 2:5-dichlorotoluene-*o*-sulphonic acid, the *p*-salt forms 2:4:5-trichlorotoluene-*o*-sulphonic acid.

C. H. D.

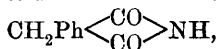
Phenylacenaphthylmethane. CHARLES DZIEWONSKI and ELIGIO DORTA (*Bull. Soc. chim.*, 1904, [iii], 31, 373—381. Compare Abstr., 1903, i, 431, and this vol., i, 84).—When a mixture of acenaphthene, benzyl chloride, and powdered zinc chloride is warmed first at 125° and, after the action has moderated, at 160 — 180° for two hours,

phenylacenaphthylmethane, $CH_2Ph \cdot C_{10}H_5 \begin{smallmatrix} \diagup CH_2 \\ \diagdown CH_2 \end{smallmatrix}$, is produced. This is isolated by distilling the reaction mixture and fractionating that portion of the distillate which boils from 320 — 360° . It crystallises from boiling alcohol in silky, white needles, melts at 112 — 113° , boils from 340 — 345° , and is soluble in ether or benzene. The *picric acid* compound is red and very unstable.

On oxidation in acetic acid solution at 85° with sodium dichromate, phenylacenaphthylmethane furnishes a mixture of *benzyl-naphthalic acid*, $CH_2Ph \cdot C_{10}H_5(CO_2H)_2$, and *benzoyl-naphthalic acid*,



The *anhydride* of the first of these can be prepared by heating the mixture of acid and anhydride first isolated at 160 — 165° ; it crystallises from boiling acetic acid and melts at 175° . The *imide*,



forms yellow needles and melts at 227° .

The *anhydride* of benzoyl-naphthalic acid is almost insoluble in boiling alcohol, crystallises from acetic acid in prisms, and melts at 196° ; the *oxime* is deposited from solutions in acetic acid as yellow prisms and melts and decomposes at 242° ; the *imide* separates from acetic acid or boiling benzene in needles and melts at 252° . It is

impossible at present to say whether this acid is identical or not with the 4-benzoylnaphthalic acid described by Graebe and Haas (Abstr., 1903, i, 409). T. A. H.

Nitration of Anthracene. JAKOB MEISENHEIMER and EDMUND CONNERADE (*Annalen*, 1904, 330, 133—184. Compare Abstr., 1901, i, 135; 1902, i, 795).—A further study has been made of the nitration of anthracene under a variety of conditions, and much of the work of Liebermann and Lindemann (Abstr., 1881, 99) and Liebermann and Landshoff (Abstr., 1881, 606) and of A. G. Perkin and Mackenzie (Trans., 1891, 59, 634; 1892, 61, 854) has been repeated. It has been found that the substances described by Liebermann and his collaborators were in many cases mixtures, and that the constitution assigned to them was not in accord with the results of the renewed investigation.

When concentrated nitric acid is added to a solution of anthracene in acetic acid, and water slowly poured into the cooled mixture, a semi-solid mass separates, from which, by dissolving in ether, *nitro-dihydroanthranlyl acetate*, $\text{OAc} \cdot \text{CH} \langle \text{C}_6\text{H}_4 \rangle \text{CH} \cdot \text{NO}_2$ (compare Dimroth, Abstr., 1901, i, 197), separates in colourless prisms melting and decomposing at 120° . It is thought that this substance is formed from the nitroanthranol, $\text{OH} \cdot \text{CH} \langle \text{C}_6\text{H}_4 \rangle \text{CH} \cdot \text{NO}_2$, which is first produced by addition of nitric acid to the anthracene. This anthranol can be esterified by a variety of acids. Thus, when nitrous fumes are led into a solution of anthracene in a mixture of acetic and nitric acids, *nitro-dihydroanthranlyl nitrite*, $\text{NO}_2 \cdot \text{CH} \langle \text{C}_6\text{H}_4 \rangle \text{CH} \cdot \text{NO}_2$, separates as colourless needles melting and decomposing at 125° . This substance is also obtained from the acetate by the action of nitrous fumes on its solution in acetic acid. The acetate can also be converted into the chloride by the action of hydrochloric acid (Dimroth, *loc. cit.*). When the solution of the acetate in acetic anhydride is treated with sulphuric acid, or the acetate is heated with sodium hydroxide, it is converted into nitroanthracene (compare Dimroth, *loc. cit.*).

Nitro-dihydroanthranlyl nitrate is prepared by adding nitric acid to a suspension of anthracene in chloroform; the hydrocarbon dissolves, and white crystals of the nitrate separate; it melts and decomposes at 78 – 79° . Both the nitrate and nitrite easily pass into nitroanthrone. With methyl alcohol, they yield the methyl ether of nitro-dihydroanthranol (m. p. 180°), and with ethyl alcohol the corresponding ethyl ether.

Trinitro-dihydroanthracene, $\text{NO}_2 \cdot \text{CH} \langle \text{C}_6\text{H}_4 \rangle \text{C}(\text{NO}_2)_2$, is formed, together with nitroanthrone, when a solution of anthracene in acetic and nitric acids is kept for some time; a similar mixture is obtained when nitrous fumes are passed into the methyl ether of nitro-dihydroanthranol; it is probably formed in both cases by the action of nitrous fumes on nitroanthracene. It is prepared by passing nitrous fumes

into a solution of nitroanthracene in chloroform, and crystallises in colourless prisms melting and decomposing at 139—140°; by sodium hydroxide, it is quantitatively converted into dinitroanthracene (m. p. 294°) and nitrous acid, but no ready exchange of a nitro-group for methoxyl takes place under the influence of methyl alcohol.

By the action of excess of nitric acid on a solution of anthracene in acetic acid, a mixture of trinitrodihydroanthracene and nitroanthrone is mainly obtained, together with small quantities of dinitroanthracene and anthraquinone.

9-Nitro- and 9:10-dinitro-anthracenes are obtained when a solution of pure nitric acid free from nitrous acid, in acetic acid and acetic anhydride, is added to a suspension of anthracene in acetic acid at 15—20°; after 24 hours, the solid is collected and the two nitroderivatives separated by alcohol, in which the dinitro-compound is insoluble. The mononitro-compound yields 9-aminoanthracene on reduction with stannous chloride in acetic acid solution; the *acetyl* derivative melts at 273—274°. The dinitroanthracene, which is identical with the nitrosonitroanthrone of Liebermann and Perkin, is best prepared by the action of sodium hydroxide on trinitrodihydroanthracene; on reduction, either 9-aminoanthracene or 9-amino-dihydroanthracene are formed, but not the 9:10-diaminoanthracene. It is changed by boiling with a methyl-alcoholic solution of potassium methoxide, the *potassium* salt, $\text{C(OMe)}_2\text{C}_6\text{H}_4\text{C:NO}\cdot\text{OK}$, being formed, since when sodium hypobromite is added to the solution, bromonitroanthrone dimethylacetal (m. p. 139°) is obtained.

By the action of nitric acid on dihydroanthracene, Liebermann and Landshoff (*loc. cit.*) obtained a dihydroanthracene nitrite; it is, however, now found that this material is a mixture of trinitrodihydroanthracene and nitroanthrone; by alkali hydroxides, the former is converted into dinitroanthracene.

All attempts to prepare Liebermann and Lindemann's "anthracene nitrite" and "hyponitrate" by the action of nitrous fumes on a chloroform solution or suspension of anthracene were unsuccessful; it appears that these authors obtained impure nitrodihydroanthranil nitrite, but the only substance which was isolated was dinitrodihydroanthracene, $\text{NO}_2\cdot\text{CHC}_6\text{H}_4\text{CH}\cdot\text{NO}_2$; it is sparingly soluble and melts at 194°, and is immediately converted by aqueous sodium hydroxide into nitroanthracene.

The action of nitric acid on ethyldihydroanthracene is analogous to its action on anthracene; in this case, nitroethyldihydroanthranol, the homologue of the unknown nitrodihydroanthranol, can be isolated. When ethyldihydroanthracene in solution in acetic acid is treated with nitric acid, a mixture of trinitroethyldihydroanthracene and nitroethyldihydroanthracene are formed; benzene extracts the trinitro-derivative from the mixture; the mononitro-derivative crystallises in long, colourless prisms melting and decomposing at 166°; it is soluble in alkali hydroxides, but by mineral acids it is converted into nitroethylantracene, which appears to be identical with Liebermann and Landshoff's nitrosoethylantrhone; it crystallises in yellow prisms melt-

ing at 135° , and is readily reduced in alcoholic solution by zinc dust and ammonium chloride to the corresponding base, which, however, is unstable and was isolated as the *acetyl* derivative; the latter forms pale yellow needles melting at $259-260^{\circ}$.

The trinitroethyldihydroanthracene, obtained by Liebermann and Landshoff from ethyldihydroanthracene, can more easily be prepared by passing nitrous fumes into an ethereal solution of nitroethylantracene. Nitroethylanthrone was found in the mother liquors in the nitration; it was also found by Liebermann and Landshoff.

Nitroanthrone (Perkin and Mackenzie, *loc. cit.*) cannot be acetylated; under the influence of alkalis, it is converted into the salts of *isonitroanthrone*, $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{C} \cdot \text{NO} \cdot \text{OH}$, which is prepared by adding dilute sulphuric acid to an ice-cold solution of the sodium salt; it crystallises in scarlet needles, which begin to decompose at 70° , and at $80-85^{\circ}$ has completely changed into the colourless nitroanthrone (m. p. 135°), a small quantity of anthraquinone being at the same time formed; it is stable in the dark, but in contact with water or acids rapidly changes into nitroanthrone. The *sodium* salt, prepared by dissolving nitroanthrone in hot concentrated sodium carbonate, crystallises in deep red leaflets, which rapidly decompose in moist air. The *silver* salt is a very unstable orange-red powder, which reacts quickly with methyl iodide, but no methyl derivative could be isolated. *Bromonitroanthrone*, $\text{NO}_2 \cdot \text{CBr} \langle \text{C}_6\text{H}_4 \rangle \text{CO}$, is obtained when sodium hypobromite is added to a solution of the sodium salt, and forms colourless crystals melting and decomposing at 116° .

It is noteworthy that all compounds of the type of nitro-, dinitro-, nitroethyl-anthracene are intensely yellow, whilst those of the type of bromonitroanthrone are colourless and compounds of the type of *iso*-nitroanthrone are red.

All attempts to obtain the methyl ether of aminoanthranol by reducing the corresponding nitro-compound were unsuccessful; a very unstable basic substance was alone formed when zinc in the presence of ammonium chloride was the agent; stannous chloride lead to the formation of anthranol.

Nitroanthrone dimethylacetal, $\text{NO}_2 \cdot \text{CH} \langle \text{C}_6\text{H}_4 \rangle \text{C}(\text{OMe})_2$, is prepared by dissolving the methyl ether of nitroanthranol in a concentrated solution of potassium methoxide in methyl alcohol, and then carefully acidifying with acetic acid, when the acetal separates; it crystallises in colourless needles melting and decomposing at 135° , and is generally contained in crude nitroanthranol methyl ether. K. J. P. O.

Preparation of *p*-Nitroaniline. THE CLAYTON ANILINE CO. (D.R.-P. 148749).—*p*-Nitroaniline is readily prepared in a pure condition by heating *p*-chloronitrobenzene with an excess of ammonia at $130-180^{\circ}$, the lower temperature being sufficient when a large excess of ammonia is employed. The yield is quantitative. The reaction is hastened by the use of dilute alcohol in place of water as a solvent.

C. H. D.

Equivalence of Positions 2 and 6 in the Benzene Nucleus.
 EMILIO NOELTING (*Ber.*, 1904, 37, 1015—1028).—The equivalence of positions 2 and 6 in the benzene nucleus is shown by the following five series of experiments.

I. 6-Nitro-2-aminotoluene is converted into 2-chloro-6-nitrotoluene (Green and Lawson, *Trans.*, 1891, 59, 1013), which, on reduction, yields 2-chloro-6-aminotoluene (Wynne and Greeves, *Proc.*, 1895, 11, 151), convertible by the diazo-reaction into 2-chloro-6-hydroxytoluene, crystallising from water in long, white needles and melting at 86°. The same compound is obtained by converting 6-nitro-2-aminotoluene into Ullmann's 6-nitro-2-hydroxytoluene and 6-amino-2-hydroxytoluene (*Abstr.*, 1884, 1316) and treating the latter with nitrous acid and cuprous chloride. Both products were identified by their giving on nitration the same mixture of 2-chloro 5-nitro-6-hydroxytoluene melting at 64.5° and 2-chloro-3-nitro-6-hydroxytoluene melting at 135°. The former of these is volatile with steam and crystallises from alcohol; the latter is non-volatile and crystallises from water.

II. 2-Bromo-6-nitrotoluene, obtained from 6-nitro-*o*-toluidine by the diazo-reaction, crystallises from alcohol in yellowish-white needles, melts at 41°, and on reduction gives 2-bromo-6-aminotoluene as a yellow oil boiling at 253—255°; the *acetyl* derivative forms white needles melting at 158°, and the *sulphate* melts at 256°. The bromotoluidine is converted by diazotisation into 2-bromo-6-hydroxytoluene, which crystallises from water in long, white needles, melts at 95°, and gives a *benzoyl* derivative melting at 76°; the *azo*-compound, prepared by interaction with diazotised *p*-nitroaniline, melts at 215°. On nitration, 2-bromo-6-hydroxytoluene gives a mixture of 2-bromo-5-nitro-6-hydroxytoluene melting at 64° and 2-bromo-3-nitro-6-hydroxytoluene melting at 145.5°. 6-Bromo-2-hydroxytoluene, prepared by the diazo-reaction from 6-amino-*o* cresol, obtained by the reduction of 6-nitro-*o*-cresol, is identical in every respect with the 2-bromo-6-hydroxytoluene already described, and gives the same products of nitration.

III. 2-Iodo-6-nitrotoluene, prepared from 6-nitro-*o*-toluidine, separates from ether in thick, yellowish-white crystals, melts at 35.5°, and on reduction gives 2-iodo-6-aminotoluene as a colourless oil; the *hydrochloride* melts and decomposes at 254°, and the *acetyl* derivative forms white needles melting at 166°. 2-Iodo-6-hydroxytoluene is volatile with steam, crystallises in long, silky needles melting at 90°, and is identical with the substance obtained from 6-amino-2-hydroxytoluene.

IV. 6-Nitro-2-cyanotoluene separates from alcohol in white crystals and melts at 69.5°; 6-amino-2-cyanotoluene crystallises from water in white needles and melts at 95.5°. 6-Chloro-2-cyanotoluene melts at 19°, boils at 107° under 28 mm. pressure, and on hydrolysis gives 6-chloro-*o*-toluic acid, which crystallises from alcohol in slender needles and melts at 159°. 2-Chloro-6-cyanotoluene, prepared from 2-chloro-6-toluidine, is identical with 6-chloro-2-cyanotoluene and gives the same acid on hydrolysis.

V. 2-Cyano-6-hydroxytoluene, prepared from 2-cyano-6-aminotoluene, crystallises from water in white needles, melts at 195°, and is identical with 6-cyano-2-hydroxytoluene obtained from 6-amino-2-hydroxytoluene.

W. A. D.

Aryl-substituted β -Naphthylamines and their Preparation by the Sulphite Method. HANS BUCHERER and A. STOHMANN (*Zeit. Farb. Text. Chem.*, 1904, 3, 57—62 and 77—81. Compare Abstr., 1903, i, 627).—The following compounds were prepared by dissolving the naphthol or naphthylamine derivative in a minimum of water and gradually adding the sodium hydrogen sulphite to the solution heated on a water-bath. Phenyl- β -naphthylamine is obtained from β -naphthol and aniline, but the yield is poor. 2-Anilinonaphthalene-6-sulphonic acid, prepared from aniline and β -naphthol-6-sulphonic acid, crystallises in colourless leaflets; the solubility in boiling water of the sodium salt is 1 : 22, of the aniline salt 1 : 20, and of the *p*-toluidine salt 1 : 65. 2-o-Tolylaminonaphthalene-6-sulphonic acid, prepared from *o*-toluidine and β -naphthol-6-sulphonic acid, forms reddish-white leaflets and is soluble in 67 parts of boiling water; the analogous *p*-tolyl derivative dissolves in 6 parts, and the *m*-xylol derivative in 4.5 parts of boiling water. 2-p-Hydroxyanilinonaphthalene-6-sulphonic acid, prepared from *p*-aminophenol, is insoluble in boiling water; 2-p-ethoxyanilinonaphthalene-6-sulphonic acid, from *p*-phenetidine, forms brownish-red leaflets and dissolves in 50 parts of boiling water. 2-p-Aminoanilinonaphthalene-6-sulphonic acid, obtained from *p*-phenylenediamine, is a grey, crystalline powder soluble in 15 parts of boiling water; sodium 2-p-sulphoanilinonaphthalene-6-sulphonate, $\text{SO}_3\text{Na} \cdot \text{C}_{10}\text{H}_6 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$, prepared from sulphanilic acid and β -naphthol-6-sulphonic acid, forms red crystals which dissolve in 3 parts of boiling water. Metanilic acid gives the analogous 2-m-sulphoanilinonaphthalene-6-sulphonic acid, soluble in 3 parts of boiling water.

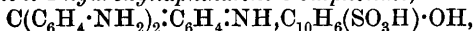
2-Anilinonaphthalene-8-sulphonic acid, prepared from aniline and croceic acid, is easily soluble in water, and not sparingly so, as stated in D.R.-P. 70349. 2-p-Tolylaminonaphthalene-8-sulphonic acid forms yellowish-green crystals which dissolve in 14 parts of boiling water. 2-p-Hydroxyanilinonaphthalene-8-sulphonic acid is a crystalline powder with a solubility 1 : 15 at 100°. 2-p-Ethoxyanilinonaphthalene-8-sulphonic acid is a greenish-grey, crystalline powder soluble in 40 parts of boiling water. 2-p-Tolylaminonaphthalene-6 : 8-disulphonic acid forms greenish-yellow crystals and is extremely soluble in water.

2-Anilinonaphthalene-6-sulphonic acid was also prepared from β -naphthylamine-6-sulphonic acid and aniline. 2-Anilino-5-hydroxynaphthalene-7-sulphonic acid, prepared from aniline and 2-amino-5-hydroxynaphthalene-7-sulphonic acid, forms snow-white crystals. 2-Anilino-8-hydroxynaphthalene-6-sulphonic acid, prepared from 2-amino-8-hydroxynaphthalene-6-sulphonic acid (" γ -acid"), crystallises in white leaflets and is soluble in 35 parts of boiling, and 300 parts of cold water. 2-p-Hydroxyanilino-8-hydroxynaphthalene-6-sulphonic acid, obtained from " γ -acid" and *p*-aminophenol, is soluble in 24 parts of boiling water; the analogous *p*-ethoxy-derivative was prepared by using *p*-phenetidine in place of *p*-aminophenol.

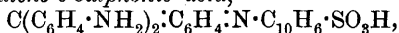
When 2-hydroxynaphthalene-3-carboxylic acid is heated with aniline under the foregoing conditions, phenyl- β -naphthylamine is obtained, not its carboxylic acid; the yield is 60 per cent. of the theory, and the method is the best available for preparing the base. The same carboxylic acid, when heated with *p*-aminophenol, gives 2-p-hydroxyanilinonaphthalene, which crystallises from a mixture of 3 parts of

alcohol and 2 of water in silver-grey leaflets with a metallic lustre and melts at 135°. 2-Anilino-8-hydroxynaphthalene-6-sulphonic acid (*supra*) was obtained from 2:8-dihydroxy-6-sulphonaphthalene-3-carboxylic acid and aniline, and the analogous 2-*p*-ethoxyphenyl derivative by using *p*-phenetidine instead.

Pararosanine 2-hydroxynaphthalene-6-sulphonate,



prepared from β -naphthol-6-sulphonic acid and pararosanine, forms lustrous, green crystals; at the same time the sparingly soluble 2-*para*-rosanilnonaphthalene-6-sulphonic acid,



is formed in much larger amount; it forms dark brown crusts with a red, metallic sheen or a finely crystalline powder, and is also obtainable from β -naphthylamine-6-sulphonic acid. W. A. D.

8-Chloro- α naphthylamine and its Sulphonic Acids. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 147852).—The azimino-compounds obtained by the action of nitrous acid on 1:8-diamino-derivatives of naphthalene react readily with hydrochloric acid in presence of copper or cuprous salts, forming 8-chloro- α -naphthylamine derivatives. Hydrogen chloride is passed into a mixture of the azimino-compound with hydrochloric acid until saturated, and copper paste is then added.

8-Chloro- α -naphthylamine-3:6-disulphonic acid, from the azimino-compound of naphthylene-1:8-diamine-3:6-disulphonic acid, crystallises in slender needles; it is diazotisable, and yields 8-amino- α -naphthol-3:6-disulphonic acid on fusion with an alkali hydroxide, whereas on heating with dilute sulphuric acid under pressure, it furnishes 8-chloro- α -naphthol-3:6-disulphonic acid, which gives rise to 1:8-dihydroxy-naphthalene-3:6-disulphonic ("chromotrope") acid when fused with an alkali hydroxide. C. H. D.

Thiodiacylanilides. GEORGE S. JAMIESON (*J. Amer. Chem. Soc.*, 1904, 26, 177—183).—The compound obtained by Tschugaeff (*Abstr.*, 1902, i, 604) by the action of potassium xanthate on benzanilidimide chloride shows no tendency to undergo molecular rearrangement and can be heated above its melting point without change. When heated with strong ammonia, it suffers decomposition with formation of thiobenzanilide and a small quantity of phenylthiourethane,



If it is treated with concentrated hydrochloric acid, benzanilide is produced. It is therefore concluded that this compound has the constitution $\text{CSPH}\cdot\text{NPh}\cdot\text{CS}\cdot\text{OEt}$.

Benzoylthiobenzanilide, $\text{CSPH}\cdot\text{NPhBz}$, obtained by the interaction of potassium thiobenzoate and benzanilidimide chloride, crystallises from alcohol in bright red prisms, melts at 108—109°, and is decomposed by boiling hydrochloric acid with formation of thiobenzanilide. This compound can also be obtained by the action of benzoyl chloride on the sodium salt of thiobenzanilide.

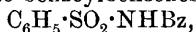
p-Bromobenzoylthiobenzanilide, $\text{CSPH}\cdot\text{NPh}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Br}$, prepared by the action of potassium *p*-bromothiobenzoate on benzanilidimide chloride, crystallises from alcohol in slender, orange-coloured prisms and melts at 120—121°.

Benzoylthio-p-bromobenzanilide, $C_6H_4Br \cdot CS \cdot NPhBz$, formed by the interaction of *p*-bromobenzanilidide chloride and potassium thio-benzoate, crystallises in slender, red prisms, melts at $133-134^\circ$, and is not changed by heating at 140° for 5 minutes. *p*-Bromothiobenzanilide, obtained from the mother-liquor from this reaction, is readily soluble in hot alcohol and melts at $161-162^\circ$.

The compound, $NPh \cdot CPh \cdot N(C_7H_7) \cdot CSPh$, obtained by the action of benzanilidide chloride on sodium thiobenzo-*p*-toluidide, forms yellow crystals, melts at $198-201^\circ$, and is very soluble in benzene or amyl acetate. The same compound may be prepared by the action of benzoyl-*p*-toluidide on the sodium salt of *p*-thiobenzanilide.

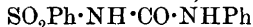
The compound, $NPh \cdot CPh \cdot NPh \cdot CSPh$, formed by the interaction of benzanilidide chloride and sodium thiobenzanilide, crystallises in yellow prisms and melts at $202-204^\circ$. E. G.

Action of Silver Cyanate on Acyl Chlorides. III. OTTO C. BILLETER (*Ber.*, 1904, 37, 690—696. Compare *Abstr.*, 1902, i, 821).—*Benzenesulphoncarbimide*, $C_6H_5 \cdot SO_2 \cdot N \cdot CO$, prepared by heating together benzenesulphonic chloride and silver cyanate, is a colourless, mobile liquid which boils at 129.6° under 9 mm., at 139.4° under 13.5 mm. pressure, and does not solidify at -22° ; it has a sp. gr. 1.369° at $19^\circ/4^\circ$. It is rapidly decomposed by water, giving carbon dioxide and benzenesulphonamide; concentrated sulphuric acid gives carbon dioxide and benzenesulphonamide sulphate. Hydrogen chloride is without action, but hydrogen iodide forms an unstable additive compound, $SO_2Ph \cdot N \cdot CO \cdot HI$. Aluminium chloride in benzene solution converts the carbimide into benzoylbenzenesulphonamide,



small quantities of diphenylsulphone being also formed.

Alcohol converts the carbimide into *ethyl benzenesulphonylcarbamate*, $SO_2Ph \cdot NH \cdot CO \cdot OEt$, which crystallises from alcohol in small plates and melts at 109° ; the sodium salt, $SO_2Ph \cdot NNa \cdot CO_2Et$, is crystalline. *Phenyl benzenesulphonylcarbamate*, $SO_2Ph \cdot NH \cdot CO_2Ph$, prepared by the interaction of the carbimide with phenol, crystallises from water and melts at 123° . With ammonia, *benzenesulphonylcarbamide*, $SO_2Ph \cdot NH \cdot CO \cdot NH_2$, is obtained; it crystallises in felted, hair-like needles melting at 167.4° . With aniline, the compound



is obtained as a crystalline powder melting at 158.4° ; the compound $SO_2Ph \cdot NH \cdot CO \cdot NPhEt$, prepared from ethylaniline, melts at 123.2° .

Benzenesulphonylacetylcarbamide, $SO_2Ph \cdot NH \cdot CO \cdot NHAc$, prepared from acetamide, forms small plates and melts at $155-156^\circ$; the analogous *benzenesulphonylbenzoylcarbamide*, obtained from benzamide, forms silky needles and melts at 208° . *Dibenzenesulphonylcarbamide*, $CO(NH \cdot SO_2Ph)_2$, prepared from benzenesulphonamide, crystallises from alcohol in long, colourless prisms and melts at 159° . W. A. D.

Behaviour of Salol and Betol towards Various Solvents. VALERIO LUSINI (*L'Orosi*, 1903, 26, 80—85).—Salol is soluble in methyl, ethyl, *n*-propyl, butyl, or amyl alcohol, amylene hydrate, ethylene glycol, mannitol, ether, light petroleum, chloroform, benzene, carbon

disulphide, acetaldehyde, methylal, acetal, or acetone; it dissolves only slightly in glycerol, whether concentrated or diluted with water. Its alcoholic solution gives, with ferric chloride, the violet coloration characteristic of the phenols; this reaction is also yielded by its solutions in all the above-named monohydric alcohols, and in acetal, acetaldehyde, and acetone; in the other solvents and also in water, however, the reaction is not obtained. In water containing only 0.25—0.35 per cent. of alcohol, salol shows the phenol reaction; so that, assuming the reaction to be due to the resolution of the salol, the presence in the organism of alcoholic liquors would be sufficient to bring about this resolution.

Betol (β -naphthyl salicylate) is absolutely insoluble in water, but dissolves in the monohydric alcohols named above, the solubility decreasing as the molecular weight increases; it is soluble also in acetaldehyde, ether, chloroform, benzene, carbon disulphide, &c., but does not dissolve in ethylene glycol, glycerol, or mannitol. In this case, the colorations obtained with ferric chloride are much less intense and more transitory than with salol. The reaction is fairly marked in methyl or ethyl alcohol, but diminishes in intensity for the higher alcohols; it is not shown in methylal, is scarcely apparent in acetaldehyde or acetal, but is very marked in acetone solution. In aqueous alcohol of less strength than 60 per cent., betol does not give a coloration with ferric chloride. T. H. P.

Mixtures of *o*-Nitrophenol and Naphthalene. A. V. SAPOSCHNIKOFF and P. HELWIG (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 1084—1097).—Melting point curves and tables of mixtures of *o*-nitrophenol and naphthalene show that these compounds dissolve one another in the liquid state, but do not form solid solutions. The melting point curve consists of two parts, which meet in a eutectic point at about 29.7°, corresponding with a mixture containing 67.2 per cent. (mols.) of the nitrophenol.

On comparing the curves for mixtures of naphthalene with picric acid, 2:4-dinitrophenol (see two following abstracts), or *o*-nitrophenol, it is seen that a fall in the number of nitro-groups in the substituted phenol shows itself in the character of the diagram obtained. The formation of a molecular compound of naphthalene and 2:4-dinitrophenol is not so clearly indicated in the melting point curve as in the case of picric acid. T. H. P.

Mixtures of 2:4-Dinitrophenol and Naphthalene. A. V. SAPOSCHNIKOFF and P. HELWIG (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 1075—1084).—The melting point diagrams and tables for mixtures of 2:4-dinitrophenol and naphthalene show that these substances unite in molecular proportions to form a compound which melts at 91.7°; this melting point is lowered by the addition of either of the constituent compounds. Besides the first solidifying point, all mixtures of 2:4-dinitrophenol and naphthalene have a second, which is that of complete solidification, and has the same value for mixtures containing the same proportion more or less than 50 per cent. (mols.) of the dinitrophenol; hence these compounds do not form solid solutions, but, from molten mixtures of them, the constituent which is present in

excess first crystallises out, and, when the liquid has reached the eutectic composition, crystallisation of the second constituent begins.

T. H. P.

Mixtures of Picric Acid and Naphthalene. A. V. SAPOSCHNIKOFF AND W. RDULTOWSKY (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 1073—1074).—The authors have determined the melting point curve of mixtures of picric acid and naphthalene. Starting from 80°, the melting point of pure naphthalene, the curve falls to a eutectic point 77·5° for a mixture containing 12·3 per cent. (mols.) of picric acid; it then rises continuously to 149·5°, when the mass contains molecular proportions of the two constituents. After this it falls to another eutectic point, 115°, the percentage (mols.) of naphthalene being then 8·59; finally, it rises to 122·5°, the melting point of picric acid. A molecular compound, melting at 149·5°, of naphthalene and picric acid is thus formed, and this may be also obtained by mixing the two constituents in molecular proportions in alcoholic solution. The points 77·5° and 115° correspond with eutectic mixtures of the molecular compound and naphthalene and picric acid respectively.

T. H. P.

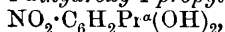
[4-Chloro-2-aminophenolsulphonic Acid.] AKTIEN-GESELLSCHAFT FÜR ANILINFABRIKATION (D.R.-P. 148198).—Sodium hydrogen sulphite converts 4-chloro-2-nitrophenol into 4-chloro-2-aminophenolsulphonic acid, crystallising in slender, transparent, prismatic needles. It is isomeric with the acid obtained on sulphonating 4-chloro-2-aminophenol, which is more readily soluble in water and crystallises in felted aggregates at the surface of the solution. The acid prepared by means of sulphite forms soluble azo-compounds when diazotised and combined with 8-amino-*a*-naphthol-2:4- or -3:6-disulphonic acid.

C. H. D.

Mixtures of Trinitrocresol and Naphthalene. A. V. SAPOSCHNIKOFF AND W. RDULTOWSKY (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 1097—1098).—Mixtures of trinitrocresol and naphthalene give a melting point curve similar to that obtained with picric acid and naphthalene. The molecular compound formed, which melts at 124·5°, may also be prepared by mixing the constituents in alcoholic solution.

T. H. P.

Derivatives of Safrole, and its Relations to the Phenol Ethers, Eugenole and Asarone. HERMANN THOMS and A. BLITZ (*Arch. Pharm.*, 1904, 242, 85—94. Compare *Abstr.*, 1903, i, 415, 558; 1904, i, 47).—*Nitrodihydrosafrole* (6-nitro-3:4-methylenedioxy-1-propylbenzene), $\text{NO}_2\cdot\text{C}_6\text{H}_2\text{Pr}^a\cdot\text{O}_2\cdot\text{CH}_2$, is obtained by adding 45 per cent. nitric acid gradually to an acetic acid solution of dihydrosafrole (Ciamician and Silber, *Abstr.*, 1890, 966); it is yellow and melts at 36°. By treatment with aluminium chloride in the presence of carbon disulphide (Hartmann and Gattermann, *Abstr.*, 1893, i, 152), it is converted into 6-nitro-3:4-dihydroxy-1-propylbenzene,



melting at 73°; this, when methylated with methyl sulphate (Ullmann, Abstr., 1900, i, 619; 1903, i, 395), gives the 6-nitro-3:4-dimethoxy-1-propylbenzene, melting at 81°, already described (Abstr., 1903, i, 415). The position of the nitro-group is thus established. When the last substance is hydrolysed by means of aluminium chloride, two products are obtained. One melts at 52°, and, when heated at 130° with ethyl iodide, gives a yellow *derivative* melting at 60°; this, on reduction with amalgamated aluminium, yielded an amine, by the oxidation of which with sodium dichromate and dilute sulphuric acid at 0° a quinone melting at 111°, already described (Abstr., 1903, i, 416), was obtained: the product melting at 52° is thus 6-nitro-3-hydroxy-4-methoxy-1-propylbenzene, $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Pr}^a(\text{OMe}) \cdot \text{OH}$. The second product melts at 78° and has the composition $\text{C}_{10}\text{H}_{13}\text{O}_4\text{N}, \text{H}_2\text{O}$; with ethyl iodide, it forms a *derivative* melting at 76°; it is presumably the 4-hydroxy-3-methoxy-isomeride of the other product.

Nitrodihydrosafrole is reduced by amalgamated aluminium (H. Wislicenus, Abstr., 1896, i, 671) to *aminodihydrosafrole* (6-amino-3:4-methylenedioxy-1-propylbenzene); this is an unstable substance, melting at 24° and boiling at 156° under 11·5 mm. pressure; its *hydrochloride* melts and decomposes above 200°; its *acetyl* derivative, prepared by means of thioacetic acid (Pawlewski, Abstr., 1898, i, 362; 1902, i, 209), melts at 171·5°, its *benzoyl* derivative at 151°; by the diazo-reaction, it can be converted into 6-hydroxy-3:4-methylenedioxy-1-propylbenzene, which melts at 71—72°.

Fuming nitric acid at 20° converts nitrodihydrosafrole into *di-* (not *tri-*) *nitrodihydrosafrole* (2:6-dinitro-3:4-methylenedioxy-1-propylbenzene); this is yellow and melts at 121°. It is reduced by amalgamated aluminium to *diaminodihydrosafrole* (2:6-diamino-3:4-methylenedioxy-1-propylbenzene), which melts at 72°; the (mono)*hydrochloride* of this melts and decomposes at 246°, the *benzoyl* derivative melts at 248°; with nitrous acid, a brown dye is formed (meta-position of the two amino-groups). Alcoholic ammonium sulphide effects a reduction to an orange-red *nitroaminodihydrosafrole* melting at 76·5°, which, when the NH_2 is replaced by hydrogen by diazotisation in boiling alcoholic solution, gives the 2-nitro-compound melting at 36° described above, and so must be 6-nitro-2-amino-3:4-methylenedioxy-1-propylbenzene.

C. F. B.

Properties of Phenyl Ether. ALFRED N. COOK (*J. Amer. Chem. Soc.*, 1904, 26, 302—304).—Phenyl ether crystallises in large prisms or thin, white plates, melts at 26·9—27°, boils at 258·97° (corr.), and is soluble in all the usual organic solvents and slightly so in water. It dissolves to the extent of 4·9 parts in 100 parts of 87 per cent. alcohol at -10°, and is much more soluble at higher temperatures. It volatilises slowly at the ordinary temperature and more rapidly when heated. The sp. gr. of the liquid ether is 1·0535 at 40°; 1·0582 at 35°; 1·0629 at 30°; 1·0677 at 25°; 1·0724 at 20°; and 1·0773 at 15°. The solid ether has a sp. gr. 1·1508 at 10·75°. The pure substance is not affected by light, but, if impure, it gradually assumes a deep yellow colour,

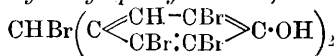
E. G.

Behaviour of Phenol Ethers on Distillation with Zinc Dust. HERMANN THOMS (*Arch. Pharm.*, 1904, 242, 95—98).—Contrary to the opinion usually held, anisole (methoxybenzene) is decomposed in part when it is mixed with zinc dust and distilled. In all, 60 grams of anisole were distilled in portions of 2·5 grams; ethylene was formed, and 20 grams of liquid distillate were obtained, from which about 3 grams each of benzene and phenol, 2·5 grams of diphenyl, and 10 c.c. of unchanged anisole were isolated. C. F. B.

Preparation of Ethers by means of Magnesium Compounds and Halogen Methyl Ethers, XCH_2OR . JULES HAMONET (*Compt. rend.*, 1904, 138, 813—814).—By a modification of Henry's method for preparing ethers from halogen methyl ethers (compare Henry, *Abstr.*, 1892, 27), namely, the substitution of Grignard's organo-magnesium compounds for the organo-zinc compounds, the author has obtained a better yield of the ether, 60—65 per cent. of the theoretical in the case of the open chain compounds, but much less in the case of the ring compounds. The reaction, which is represented by the equation $RMgX + XCH_2OR = MgX_2 + CH_2ROR$, proceeds more readily with the bromo-derivative of the methyl ether than with the chloro- or iodo-compound, and the bromomethyl ethers are prepared by the action of hydrobromic acid on the corresponding chloro-compounds. The action of bromomethyl ether, CH_2BrOMe , and bromomethyl amyl ether, $CH_2BrO \cdot C_5H_{11}$ (a liquid boiling at 74—76° under 18 mm. pressure), on the magnesium derivatives of ethyl bromide, phenyl bromide, and benzyl chloride was studied, and the following ethers were prepared: propyl amyl ether, $C_3H_7O \cdot C_5H_{11}$, boiling at 130°, benzyl methyl ether, CH_2PhOMe , boiling at 170°, and *phenylethyl methyl ether*, $OMe \cdot CH_2 \cdot CH_2Ph$, a colourless liquid boiling at 189—190°. M. A. W.

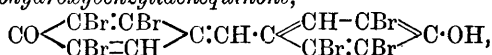
Action of Bromine and Chlorine on Phenols: Substitution Products, ψ -Bromides, and ψ -Chlorides. X. Action of Bromine on *p*-Dihydroxydiphenylmethane. THEODOR ZINCKE and R. KRÜGENER (*Annalen*, 1903, 330, 61—81).—Tetrabromo-*p*-dihydroxydiphenylmethane is readily prepared by treating dihydroxydiphenylmethane in acetic acid solution with bromine (compare Staedel, *Abstr.*, 1878, 420); it melts at 226—227°, and yields an *acetyl* derivative when acted on with acetic anhydride in the presence of sulphuric acid, which crystallises in needles melting at 167—168°. When the tetrabromide is left in contact with bromine for 24 hours, a *hexabromide*, $CH_2(C \begin{smallmatrix} \text{CH}=\text{CBr} \\ \text{CBr} \cdot \text{CBr} \end{smallmatrix} > C \cdot OH)_2$, is formed, which crystallises in colourless needles melting at 204°, and is not acted on by reducing agents or by sodium methoxide; its *diacetyl* derivative crystallises in needles melting at 215°.

*ψ -Heptabromo-*p*-dihydroxydiphenylmethane,*



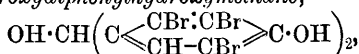
or $\text{CO} \begin{smallmatrix} \text{CBr}=\text{CH} \\ \text{CBr}:\text{CBr} \end{smallmatrix} \text{CH} \cdot \text{CHBr} \cdot \text{C} \begin{smallmatrix} \text{CH}-\text{CBr} \\ \text{CBr}:\text{CBr} \end{smallmatrix} \text{C} \cdot \text{OH}$, prepared by heating the hexabromide with excess of bromine under pressure at 100° for four hours, is purified by recrystallising from acetic acid containing hydrogen bromide, from which it separates in colourless needles or prisms melting and decomposing at $205\text{--}206^\circ$, the prismatic form showing signs of change at a lower temperature, 194° . Under a great variety of conditions, treatment with moist ether, methyl or ethyl alcohol, acetone, with aqueous sodium carbonate or acetate, with strips of various metals, zinc, &c., and with sulphuric acid, it loses hydrogen bromide, yielding a benzylidenequinone. By hydriodic acid, it is converted into hexabromodihydroxydiphenylmethane. When boiled with acetic anhydride, the ψ -bromide is converted into *diacetoxyhexabromo- ψ -diphenylbromomethane*, $\text{CHBr}(\text{C}_6\text{H}_5\cdot\text{OAc})$, which crystallises in colourless needles melting at $227\text{--}228^\circ$.

Hexabromohydroxybenzylidenequinone,



is best prepared by dissolving the ψ -heptabromide in aqueous acetone, when the solution becomes deeply coloured and a mass of crystals separates; it crystallises in small, red needles melting at 245° , and is relatively stable; it dissolves in sulphuric with a violet coloration, and readily forms additive products with hydrogen chloride and bromide, in the latter case forming the ψ -heptabromide, and in the former a ψ -hexabromochloro-compound, which crystallises in needles, melting and decomposing at $215\text{--}217^\circ$. When reduced with hydriodic acid, hexabromodihydroxydiphenylmethane is produced. It forms a series of salts which dissolve with a blue colour; the *sodium* salt is prepared by treating an acetone solution of the heptabromide with sodium carbonate and crystallises in bluish-violet metallic needles or leaflets; it is decomposed by the same agents which attack the quinone. Other salts can be prepared by precipitation from the sodium salt. Further, when strips of zinc or magnesium are immersed in an ethereal solution of the heptabromide, they become covered with crystals of the corresponding salts of the two metals.

Hexabromodihydroxydiphenylhydroxymethane,



is prepared by adding only so much water to an acetone solution of the heptabromide that the quinone is not precipitated; the original deep colour slowly disappears, and on diluting the new substance separates; it can also be obtained from the mother liquor from the preparation of the quinone; it crystallises in rhombic plates, melting and decomposing at 250° , and in slender needles melting and decomposing at 247° . It is converted by dissolution in sulphuric acid into the quinone. Its *triacetyl* derivative, which can be prepared either from the hydroxymethane or by treating the quinone with acetic anhydride and sulphuric acid, forms lustrous needles melting at 204° . Evidence of the existence of the quinonoid form of the carbinol was obtained; it forms a deep violet solution in alkali carbonates, which is rapidly decolorised by the air.

Hexabromodihydroxydiphenylmethoxymethane,
 $\text{OMe} \cdot \text{CH}(\text{C}_6\text{HBr}_3 \cdot \text{OH})_2,$

prepared by treating the heptabromide with methyl alcohol, or by warming a solution of the quinone in methyl alcohol, forms colourless, monoclinic crystals melting and decomposing at 179° . The corresponding *ethoxy*-derivative is obtained in a similar manner, and forms rhombic crystals melting at 189 – 190° . *Hexabromodihydroxydiphenyl-acetoxymethane*, produced when either the heptabromide or the quinone is treated with acetic acid, forms small crystals, melting and decomposing at 225 – 226° ; another form crystallising in needles begins to melt at 208° . With alkalis, it is converted into salts of the quinone.

K. J. P. O.

Methylene Compounds of the Phloroglucinol Series.
 RUDOLF BOEHM (*Annalen*, 1903, 329, 269–331. Compare Abstr., 1902, i, 37).—Most members of the phloroglucinol series yield, more or less readily, methylene derivatives with formaldehyde; the following substances have been investigated: phloroglucinol and its monomethyl ether, cotoin, methylphloroglucinol and its β -monomethyl ether, aspidinol (the β -methyl ether of methylphloroglucinyl-*n*-butanone), and filicic acid. 1:3:5-Trimethylphloroglucinol will not react with formaldehyde, even at a high temperature in the presence of a condensing agent. The presence of methyl groups in the nucleus increases the ease with which phloroglucinols react with formaldehyde. In the case of the monomethyl ethers of phloroglucinol, the methylene group takes up an ortho-position relatively to the methoxy-group.

Phloroglucinol and methylphloroglucinol (that is, compounds with two CH groups) yield complex dimolecular or trimolecular methylene compounds, which are unstable, and obtained crystalline only with difficulty. Those derivatives of phloroglucinol which contain only one CH group, dimethylphloroglucinol, aspidinol, and filicyl-*n*-butanone, yield well crystalline and stable methylene derivatives. From phloroglucinol, red, amorphous compounds are obtained which are insoluble in acids and alkalis. In the case of monomethyl ethers, even when two CH groups are present, only simple condensation products are formed.

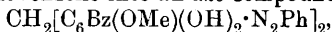
The methylene derivatives are decomposed by sodium hydroxide and zinc dust into two or four homologous phloroglucinols, according to their complexity, amorphous by-products being produced in the case of secondary phloroglucinols.

According to their behaviour with alcoholic diazoaminobenzene, these methylene compounds fall into three groups: (1) the derivatives of methylphloroglucinol and its β -monomethyl ether, and filicic acid (that is, compounds having one CH group in the nucleus), yield with two mols. of diazoaminobenzene well crystallised azo-compounds with two azo-groups corresponding with the diphenylmethane type. Further treatment with alcoholic diazoaminobenzene effects cleavage at the methylene bridge and formation of a disazo-compound. (2) Methylene derivatives which do not contain a CH group in the nucleus, such as the derivatives of dimethylphloroglucinol and filicyl-*n*-butanone, are directly decomposed, benzeneazophloroglucinols being produced,

Flavaspidic and filicic acids and albaspidin and phloraspin belong to this group. (3) Methylene derivatives not containing a CH group, and with methoxy-groups in the ortho-position relatively to the methylene group, do not react with diazoaminobenzene; to this group belongs the natural aspidin.

Phloroglucinol does not react with formaldehyde at the ordinary temperature in aqueous solution, but in the presence of 15 per cent. sulphuric or hydrochloric acids a reaction takes place, crystals rapidly separating; these crystals are not permanent. In order to obtain methylenebisphloroglucinol, 2 mols. of phloroglucinol and 1 mol. of formaldehyde must be used, and the product, which contains complex substances, shaken with water, dissolved in ether, and finally precipitated from solution in ethyl acetate by benzene, the second fraction containing the methylene derivative. Sodium hydroxide and zinc dust convert the mixture of condensation products into phloroglucinol and methylphloroglucinol (about equal quantities), a very small quantity of dimethylphloroglucinol, and somewhat more trimethylphloroglucinol. Diazoaminobenzene yields an insoluble, dark red azo-compound.

The monomethyl ether of phloroglucinol cannot only be prepared synthetically, but also by treatment of cotoin with zinc dust and sodium hydroxide; with formaldehyde, the ether condenses to form methylenebisphloroglucinol methyl ether, which is decomposed by sodium hydroxide and zinc dust, producing the β -methyl ether of methylphloroglucinol (m. p. 119°). From cotoin, methylenebiscotoin, $\text{CH}_2[\text{C}_6\text{HBz(OMe)(OH)}_2]_2$ (the "fortoin" of commerce), is readily prepared; on reduction, it yields the monomethyl ethers of phloroglucinol and of methylphloroglucinol. Methylenebiscotoin is converted by diazoaminobenzene into an azo-compound,



which forms scarlet crystals melting at 246°, and is not changed by further treatment with diazoaminobenzene.

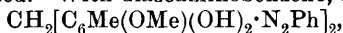
Methylphloroglucinol combines slowly with formaldehyde, but in presence of sulphuric acid it reacts very rapidly, forming a mass of minute, colourless needles, which melt and decompose at 230°; the aqueous solution of the substance, methylenebismethylphloroglucinol, gives a pale violet-red coloration with ferric chloride, and then a pale brown precipitate. On reduction, it is converted into a mixture of methyl- and dimethyl-phloroglucinols.

When methylphloroglucinol (3 mols.) is condensed with formaldehyde (2 mols.), a substance is obtained from which, on reduction, 1:3:5-trimethylphloroglucinol can be prepared.

By the action of diazoaminobenzene on methylenebismethylphloroglucinol, the azo-compound, $\text{CH}_2[\text{C}_6\text{Me(OH)}_3\cdot\text{N}_2\text{Ph}]_2$, is formed; it crystallises in brownish-black needles, which are unchanged at 290°, and on further treatment with diazoaminobenzene are converted into *methylphloroglucinoldiazobenzene*, $\text{C}_6\text{Me(OH)}_3\cdot\text{N}_2\text{Ph}$; the latter crystallises in scarlet needles and decomposes at 238°.

The β -methyl ether of methylphloroglucinol, prepared from aspidin or aspidinol, condenses readily with formaldehyde, forming the *methyl ether of methylenebismethylphloroglucinol*, $\text{CH}_2(\text{C}_8\text{H}_9\text{O}_3)_2$, which forms colourless crystals melting at 228–229°. On reduction, small

quantities of the β -methyl ethers of methyl- and dimethyl-phloroglucinols are obtained. With diazoaminobenzene, an *azo*-compound,



is obtained as dark red needles melting at $245-246^\circ$; with excess of diazoaminobenzene, the disazo-compound, $\text{C}_6\text{Me}(\text{OMe})(\text{OH})_2(\text{N}_2\text{Ph})_2$, melting at 204° , is formed.

Methylenebisaspidinol, $\text{C}_{25}\text{H}_{32}\text{O}_8$, is obtained by the action of formaldehyde on an aqueous alcoholic solution of aspidinol (the β -methyl ether of methylphloroglucinol-*n*-butanone), and crystallises in colourless prisms melting at $190-191^\circ$, and gives a green coloration with ferric chloride in alcoholic solution. On reduction, the β -methyl ethers of methyl- and dimethyl-phloroglucinols are formed: from the formation of the last-named ether, it follows that aspidinol is represented by the formula $\text{OMe} \cdot \text{C} \begin{smallmatrix} \text{CMe} \cdot \text{C}(\text{OH}) \\ \text{CH} - \text{C}(\text{OH}) \end{smallmatrix} \text{C} \cdot \text{COPr}^a$.

Filicic acid (dimethylphloroglucinol) reacts with formaldehyde only in alkaline solution, the methylene derivative, $\text{CH}_2(\text{C}_8\text{H}_9\text{O}_3)_2$, being produced; it is a colourless, amorphous powder, softening at 150° and forming a liquid above 200° . On reduction with sodium hydroxide and zinc dust, besides filicic acid, methylfilicic acid (1:1:3-trimethylphloroglucinol) is obtained, crystallising in colourless needles or prisms, which melt at $178-180^\circ$ and soon become yellow in moist air. In aqueous solution, it gives with ferric chloride a reddish-violet coloration, which changes to yellow, whilst a yellow precipitate separates. Ammoniacal silver nitrate is immediately reduced in the cold. Methylfilicic acid is less reactive than the parent substance, and does not yield crystalline derivatives with phosphorus pentachloride, acetyl chloride, or benzoyl chloride. When submitted to the action of bromine in acetic acid solution, a *dibromomethylfilicic acid*, $\text{C}_9\text{H}_{10}\text{O}_3\text{Br}_2$, is obtained, crystallising in colourless prisms melting at 142° . With excess of bromine in the presence of water, a keto-bromide, *tribromomethylfilicic acid*, $\text{CO} \begin{smallmatrix} \text{CMe}_2 \cdot \text{CO} \\ \text{CBr}_2 - \text{CO} \end{smallmatrix} \text{CMeBr}$, is formed; it crystallises in colourless needles, melting at 116° , decomposes potassium iodide, and gives no reaction with ferric chloride. By bromine and alkalis, it is profoundly changed, bromoform, carbon tetrabromide, and dimethylmalonic acid having been isolated. It is pointed out that three formulæ are possible for methylfilicic acid, differing in the relative positions of the two hydroxyl and the keto-groups.

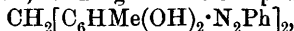
Methylenebisfilicic acid and diazoaminobenzene yield an *azo*-derivative, containing two benzeneazo-groups, $\text{C}_{29}\text{H}_{28}\text{O}_6\text{N}_4$, which crystallises in lemon-yellow needles melting at $223-224^\circ$; on further treatment with excess of diazoaminobenzene, decomposition takes place, *filicyldiazobenzene*, $\text{C}_6\text{H}_2\text{Me}_2\text{O}_3(\text{N}_2\text{Ph})_2$, being obtained as dark red crystals melting at 209° .

K. J. P. O.

Methylene Compounds and Two New Homologues of Orcinol. OSCAR SIMON (*Annalen*, 1903, 329, 301-310).—The methylene compounds of orcinol are analogous to those of phloroglucinol (preceding abstract) in that they are reduced by sodium hydroxide and zinc dust,

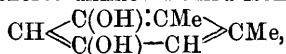
yielding derivatives of *m*-dihydroxybenzene, but they are not decomposed by diazoaminobenzene in alcoholic solution.

Methylenebisorcinol (Möhlau and Koch, Abstr., 1895, i, 46) reacts with diazoaminobenzene, forming the *azo*-compound,



which crystallises in dark red needles and is not affected by further treatment with diazoaminobenzene. Orcinol yields the *disazo*-compound, $\text{C}_6\text{Me}(\text{OH})_2(\text{N}_2\text{Ph})_2$, which crystallises in scarlet needles melting and decomposing at 229—230°.

When methylenebisorcinol is decomposed by sodium hydroxide and zinc dust, mol. proportions of orcinol and a dimethyldihydroxybenzene, which must be the hitherto unknown third isomeride,

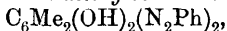


are formed; it follows from this fact that the methylene group is attached to the carbon atom in the ortho-position relatively to the hydroxyl group.

3 : 5-Dihydroxy-1 : 2-dimethylbenzene crystallises with $1\text{H}_2\text{O}$ in colourless prisms, melting when free from water at 136—137°; it yields an intense indigo-blue coloration with ferric chloride, and, on treatment with benzoylchloride by the Schotten-Baumann method, forms a *dibenzoyl* derivative, which crystallises in colourless prisms melting at 100—102°.

When acted on by excess of bromine in acetic acid, the phenol is converted into a *keto-bromide*, $\text{CBr}_2 \begin{array}{c} \text{CO} \cdot \text{CMe} \\ \text{CO} \cdot \text{CBr}_2 \end{array} \text{CMe}$, which crystallises in

pale yellow, rhombic plates or prisms, melting and decomposing at 128—129°, and is decomposed by sodium hydroxide, bromoform being produced. On digesting the phenol with diazoaminobenzene in alcoholic solution, 3 : 5-dihydroxy-1 : 2-dimethylbenzenedisazobenzene,



is formed, and crystallises in long, pale red needles melting and decomposing at 229°; from acetic acid, it crystallises with one mol. of acetic acid.

3 : 5-Dihydroxy-1 : 2-dimethylbenzene condenses with formaldehyde in the presence of sulphuric acid, forming a methylene derivative from

which 4 : 6-dihydroxy-1 : 2 : 3-trimethylbenzene, $\text{CH} \begin{array}{c} \text{C}(\text{OH}) \cdot \text{CMe} \\ \text{C}(\text{OH}) : \text{CMe} \end{array} \text{CMe}$,

is obtained on reduction with sodium hydroxide and zinc dust. It crystallises in rhombic leaflets or colourless needles melting at 163—164°; the *dibenzoyl* derivative forms colourless prisms melting at 191°. The same dihydroxytrimethylbenzene is obtained on reducing the crude methylenebisorcinol, a fact which shows that this material contains at least a trimolecular condensation product. From the constitution of the dihydroxytrimethylbenzene, it follows that both the methylene groups in the trimolecular compound must be in the ortho-position relative to the methyl group of orcinol. K. J. P. O.

Flavaspidic Acid. RUDOLF BOEHM (*Annalen*, 1903, 329, 310—320. Compare Abstr., 1902, i, 37).—When flavaspidic acid is reduced by digesting the acid (1 part) with a solution of hydriodic acid (2 parts) in acetic acid (10 parts), 45 per cent. of the original

material is obtained as an insoluble substance forming colourless crystals, which melt and decompose at 257—259° and become red in colour when kept. This substance appears to be formed by the opening of the four-membered ring (compare *loc. cit.*), the addition of two atoms of hydrogen, and the elimination of water, and consequently to have the formula

$$\text{CO} \cdot \text{CMe}_2 \cdot \text{C} \text{---} \text{O} \cdot \text{C} \cdot \text{C}(\text{COPr}^a) \cdot \text{C} \cdot \text{OH}$$

$$\text{COPr}^a \cdot \text{C} \cdot \text{C}(\text{OH}) \cdot \text{C} \cdot \text{CH}_2 \cdot \text{C} \cdot \text{C}(\text{OH}) \text{---} \text{CMe}$$
; this

anhydride is called *dihydroflavaspidyloxanthene*. By digestion with sodium hydroxide and zinc dust, one butyryl group is eliminated, and a compound, $\text{C}_{20}\text{H}_{22}\text{O}_6$, obtained, which, with 1 mol. of acetone, forms crystals melting at 213—215°. Unlike the anhydride containing two butyryl groups which cannot be benzoylated, this substance yields a benzoyl derivative, which melts at 186—187°, is insoluble in alkalis, and dissolves in alcohol with a greenish-yellow fluorescence.

Although flavaspidic acid yields acetyl derivatives when treated with acetic anhydride (compare *loc. cit.*), it does not react with acetic acid or with acetic acid containing hydrogen chloride.

Flavaspidic acid is slowly decomposed by prolonged boiling with alcohol, the *ethyl ether* of dihydroflavaspidyloxanthene

$$\text{CO} \cdot \text{CMe}_2 \cdot \text{C} \text{---} \text{O} \cdot \text{C} \cdot \text{C}(\text{COPr}^a) \cdot \text{C} \cdot \text{OH}$$

$$\text{COPr}^a \cdot \text{C} \cdot \text{C}(\text{OEt}) \cdot \text{C} \cdot \text{CH}_2 \cdot \text{C} \cdot \text{C}(\text{OH}) \text{---} \text{CMe}$$
, being formed, and crystal-

lising in red leaflets or prisms melting at 236°. The corresponding *methyl ether*, prepared by boiling the acid with methyl alcohol, crystallises in golden-yellow needles or prisms melting at 249—250°. At the same time, other substances are formed in each case; the *ethyl ether* of dihydroflavaspidic acid, $\text{C}_{24}\text{H}_{29}\text{O}_7(\text{OEt})$, crystallises in pale yellow needles melting at 198—200°, which give a greenish-brown coloration with ferric chloride, and a red coloration and a smell of butyric acid when warmed with sulphuric acid. On digestion with diazoaminobenzene, it is converted into benzeneazomethylphloroglucinyln-butanone (m. p. 181—182°). The corresponding *methyl ether* crystallises in yellow, rhombic leaflets melting at 201—202°, and yields the same azo-derivative as the ethylether when treated with diazoaminobenzene.

Methylphloroglucinyln-butanone, $\text{C}_6\text{HMe}(\text{OH})_3 \cdot \text{COPr}^a$, is also formed in each case, although in greater quantity when ethyl alcohol is used; it crystallises in colourless needles melting at 161—162°, and gives a violet-red coloration with ferric chloride, a brown precipitate afterwards separating.

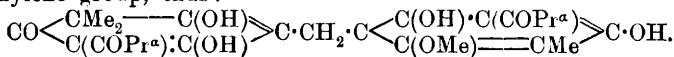
K. J. P. O.

Aspidin. RUDOLF BOEHM (*Annalen*, 1903, 329, 321—337. Compare Abstr., 1898, i, 40; 1899, i, 32, 804; 1902, i, 37).—Aspidin, which has been recently shown (Abstr., 1900, i, 49) never to be present in the extracts of *Aspidium filix mas*, but to be procurable from *Aspidium spinulosum*, is now proved to be identical with “polystichin” (compare Poulsson, Abstr., 1896, i, 387; 1899, i, 379), both the anilide, $\text{C}_{31}\text{H}_{37}\text{O}_7\text{N}$, and the compound with phenylhydrazine, $\text{C}_{37}\text{H}_{49}\text{O}_5\text{N}_4$, having the same melting points. *Acetylaspidin*, $\text{C}_{25}\text{H}_{30}\text{O}_8\text{Ac}_2$, prepared from aspidin by the action of acetic anhydride or acetyl chloride, crystallises in colourless prisms or needles melting at 108°.

Aspidin is more stable towards reagents than other members of the filicic acid group. Under the influence of sodium hydroxide and zinc dust, it is converted into filicic and methylfilicic acids, the β -methyl ether of methylphloroglucinol and butyric acid, but the reaction is not quantitative, as in the case of flavaspidic and filicic acids. A certain proportion of the aspidin always undergoes an intramolecular change, and consequently the calculated amount of butyric acid (2 mols. for each mol. of aspidin) is never obtained.

Whenever aspidin is subjected to the action of hot sodium hydroxide (with or without zinc dust), it is converted into an isomeric substance, ψ -aspidin. This compound crystallises from alcohol or petroleum in pale yellow prisms and has a double melting point; when quickly heated, it melts at 144° , but when slowly heated it either suffers no change at this temperature or only softens, to assume a crystalline habit at a higher temperature; it finally melts at 158 – 159° . Whilst aspidin contains only one methoxy-group, ψ -aspidin has two; a methyl group must therefore have wandered from a carbon to an oxygen atom. ψ -Aspidin is extremely stable towards alkalis, small quantities of the β -methyl ether of methylphloroglucinol being produced; when treated with sulphuric acid, butyric acid is set free. Towards phenylhydrazine, ψ -aspidin behaves in a similar manner to aspidin, an unstable compound, $C_{37}H_{42}O_5N_4$, being formed; it is crystalline and melts at 201 – 202° . Both aspidin and ψ -aspidin are stable towards diazoaminobenzene, a fact which shows that in neither substance is there a CH group, or a methoxy-group in an ortho-position relatively to a methylene group.

Since among the decomposition products of aspidin the two homologues, filicic and methylfilicic acid, are found, it follows that aspidin is a methylene compound; its molecule consists most probably of the two complexes, filicyl-*n*-butanone and aspidinol linked together by a methylene group, thus:



The reduction of aspidin affords further evidence for this formula. When treated at 100° with hydriodic acid in the presence of acetic acid, aspidin is converted into two substances; one is identical with dihydroflavaspidylxanthen (preceding page) and melts at 259 – 260° ; aspidin has lost a methoxy-group, and at the same time been converted into an anhydride. The other product is the anhydride of aspidin, which has lost one butyryl group; it crystallises in colourless needles melting at 216° , and exhibits a pale bluish-green fluorescence in alcoholic solution; it yields a *monobenzoyl* derivative by the Schotten-Baumann method, crystallising in colourless needles melting at 140 – 142° , and having an intense blue fluorescence in alcoholic solution.

The facts just mentioned leave little doubt that aspidin is the methyl ether of dihydroflavaspidic acid, and further confirm the suggestion (this vol., i, 406) that in the reduction of flavaspidic acid the four-membered ring is broken.

As regards the constitution of ψ -aspidin, it is probable that the

migration of the methyl group occurs in the filicyl and not in the aspidinol nucleus.

K. J. P. O.

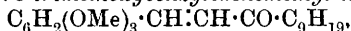
Phloraspin. RUDOLF BOEHM (*Annalen*, 1903, 329, 338—339 Compare Abstr., 1902, i, 37).—During the investigation of large quantities of the pharmacopœal extract of fern, a small amount of a new substance, *phloraspin* (0.15 per cent. of the extract), has been met with. It was obtained in the mother liquors in the preparation of flavaspidic acid and of aspidin. This compound, $C_{23}H_{28}O_8$, crystallises in colourless needles from acetone, melts at 211° , and gives a reddish-brown coloration with ferric chloride; it contains a methoxy-group and behaves towards alkalis and sulphuric acid as do filicic and flavaspidic acids, giving butyric acid. Digestion with alcoholic diazoaminobenzene decomposes phloraspin, benzeneazomethylphloroglucinol-*n*-butanone (m. p. 182°) being produced. Hence one-half of the mol. of phloraspin consists of methylphloroglucinol-*n*-butanone, and the other half, which contains the methoxyl group, of the methyl ether of phloroglucinol-*n*-butanone.

K. J. P. O.

Derivatives of Asarone. [HERMANN THOMS and] RUDOLF BECKSTROEM (*Arch. Pharm.*, 1904, 242, 98—104).—Chromyl chloride oxidises dihydroasarone to 4-methoxy-1-propyl-2 : 5-benzoquinone (Abstr., 1903, i, 415, 416), melting at 111° ; some asarylaldehyde is formed also.

Dibromoasarone is converted by methyl-alcoholic sodium methoxide in the cold into a substance, $C_{13}H_{19}O_4Br$, melting at 77.5° ; presumably this is $C_6H_5(OMe)_3 \cdot CH(OMe) \cdot CHMeBr$, the α -bromine atom having been replaced by a methoxyl group (compare Auwers and Müller, Abstr., 1902, i, 213). When dibromoasarone is kept for a long time, it becomes transformed into a substance with a percentage of bromine corresponding with $C_{24}H_{31}O_6Br$; this melts at 109.5° and is saturated in character.

Asarylaldehyde condenses with acetone in alcoholic solution, in the presence of a little sodium hydroxide, to form the yellow 2 : 4 : 5-trimethoxybenzylideneacetone, $C_6H_2(OMe)_3 \cdot CH : CH \cdot CMeO$; this melts at 96.5° , its yellow oxime at 145° . With methyl nonyl ketone in similar circumstances, 2 : 4 : 5-trimethoxybenzylidenemethyl nonyl ketone,



is formed; this melts at 97.5° , its yellow oxime at 86° , and its yellow semicarbazone at 151 — 152° ; it does not form a compound with sodium hydrogen sulphite, and consequently does not contain a $\cdot CMeO$ group.

Asarylaldehyde, when its alcoholic solution is saturated at 0° with gaseous hydrogen chloride, forms an acetal, 2 : 4 : 5-trimethoxybenzylidene diethyl ether, $C_6H_2(OMe)_3 \cdot CH(OEt)_2$, melting at 101.5° .

C. F. B.

Diphenyl-*o*- and *p*-tolyl-carbinols. SALOMON F. ACREE (*Ber.*, 1904, 37, 990—994).—Diphenyl-*p*-tolylcarbinol, $C_6H_4Me \cdot CPh_2 \cdot OH$, prepared either by the action of sodium phenoxide on phenyl *p*-tolyl ketone, or, better, by the action of magnesium *p*-tolyl bromide on benzophenone, melts at 73 — 74° , that is, considerably lower than the corresponding ortho-derivative; when oxidised, triphenylcarbinol-*p*-carboxylic

acid is formed. *Diphenyl-o-tolylcarbinol*, prepared in a similar manner from magnesium *o*-tolyl bromide and benzophenone, melts at 98° and boils at 240—245° under 24 mm. pressure. It gives a yellow coloration with sulphuric acid, which vanishes on the addition of water. *Diphenyl-m-tolylcarbinol* melts at 65°, distils at 240—245° under 19 mm. pressure, and gives a reddish-yellow coloration with sulphuric acid. E. F. A.

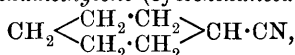
Arnisterol, the Phytosterol of Arnica Montana. TIMOTHÉE KLOBB (*Compt. rend.*, 1904, 138, 763—765. Compare Abstr., 1903, i, 165).—The author has isolated a new phytosterol (*arnisterol*) from the mixture of hydrocarbons (compare Börner, Diss., Erlangen, 1891) and arnicin, obtained by extracting the flowers of *Arnica montana* with light petroleum. *Arnisterol*, $C_{28}H_{46}O_2$, crystallises from alcohol or alcohol and benzene in well-formed rhombohedral crystals, containing 1 mol. of alcohol of crystallisation, which it loses at 115—120°; it melts at 249—250° (corr.) and sublimes at a higher temperature; is soluble in all the ordinary organic solvents, but crystallises only from alcohol, gives the colour reactions characteristic of phytosterols, and has $[\alpha]_D + 62.8'$. It reacts readily with benzoyl chloride, but no crystalline derivative has been isolated. M. A. W.

Spongosterol, a Cholesterol-like Substance from Suberites Domuncula, and its Probable Relationship to Lipochrome. MARTIN HENZE (*Zeit. physiol. Chem.*, 1904, 41, 108—124).—A cholesterol compound, *spongosterol*, $C_{19}H_{32}O$ (?), has been isolated from the ethereal alcoholic extract of *Suberites domuncula*. It crystallises from 95 per cent. methyl alcohol in glistening plates, melting at 119—120°, and has $[\alpha]_D - 19.59^\circ$. It is more readily soluble in alcohol than cholesterol, and also dissolves readily in ether, chloroform, or carbon disulphide, the ethereal solution yielding large, rhomboidal crystals. The crystals give no coloration with 20 per cent. sulphuric acid. The *acetate* melts at 124.5°, the *propionate* at 135—136°, and the *benzoate* at 128°. The *dibromide* (?) crystallises from dilute alcohol in small plates melting at 130°.

The lipochrome which accompanies spongosterol in *Suberites domuncula* has not been obtained in a crystalline form, and does not appear to be transformed, under the influence of light, into spongosterol, but gradually loses its colour owing to oxidation.

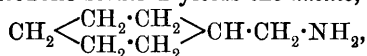
The fatty matter contained in the sponge yields, on hydrolysis, an acid, $C_{12}H_{24}O_2$ (?), melting at about 110°. J. J. S.

The Nitrile of Hexamethylenecarboxylic Acid. The Amine, $C_6H_{11}\cdot CH_2\cdot NH_2$, and its Transformation into Suberyl Alcohol. NIKOLAUS J. DEMJANOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 166—176).—*Cyanohexamethylene* (cyclohexanecarboxylonitrile),



obtained by converting cyclohexanecarboxylic acid into the chloro-

anhydride, the latter into the corresponding amide by means of aqueous ammonia, and the amide into cyanohexamethylene with phosphoric oxide, is a colourless liquid boiling at 189·5—190° under 755 mm. pressure, and solidifying to a light, crystalline mass melting at 6—7°; it has a sp. gr. 0·9268 at 15°/10°, and 0·9182 at 20°/10°. Reduction with sodium in alcoholic solution yields the *amine*,

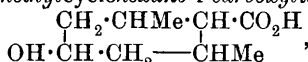


which is a colourless, viscous liquid boiling at 163° under 740 mm. pressure; it does not solidify at -15°, and its sp. gr. is 0·8896 at 0°/0°, and 0·8738 at 20°/0°; it rapidly absorbs carbon dioxide, giving a slightly soluble salt; its *hydrochloride* forms thick plates melting at about 254°; its *platinichloride* melts at about 240°, and its *picrate* at 184—186°; the *aurichloride* was also prepared. On heating the nitrite of the amine, it decomposes, yielding suberyl alcohol, which was first prepared by reduction of suberone (see Markownikoff, Abstr., 1894, i, 160). This is a case of change from a 6-carbon atom ring to one containing 7 carbon atoms. On oxidation with chromic acid, this alcohol yields suberone, whilst concentrated nitric acid converts it into pimelic acid.

T. H. P.

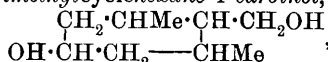
[*cycloHexane Derivatives.*] FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 148206 and 148207).—Reduction of *cyclo-Δ*²-hexene-4-one-1-carboxylic acids with sodium and alcohol yields 4-hydroxycyclohexane-1-carboxylic acids and 4-hydroxycyclohexane-1-carbinols, together with small quantities of cyclohexenecarboxylic acids.

4-Hydroxy-2 : 6-dimethylcyclohexane-1-carboxylic acid,



from 2 : 6-dimethylcyclohexene-4-one-1-carboxylic acid, is obtained as an oily mixture of two geometrical isomerides. When distilled under reduced pressure, two *lactones*, C₉H₁₄O₂, are obtained, both of which boil at 129—131° under 12 mm. pressure. The γ-lactone is solid, and the δ-lactone liquid. The *ethyl* ester, OH·C₈H₁₄·CO₂Et, is obtained from the potassium salt and ethyl iodide, and boils at 144—146° under 16 mm. pressure.

4-Hydroxy-2 : 6-dimethylcyclohexane-1-carbinol,



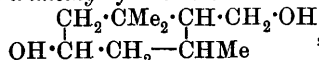
is a very viscous oil boiling at 159—161° under 14 mm. pressure, and dissolving readily in water. It is a mixture of two geometrical isomerides. The *diacetyl* derivative, C₁₃H₂₂O₄, is an insoluble oil boiling at 160° under 13 mm. pressure.

Ethyl 2 : 6 : 6-Trimethylcyclo-Δ²-hexene-4-one-1-carboxylate (this vol., i, 317) yields, on reduction, a mixture of hydroxy-acid and carbinol in the proportion 3 : 1. The crude 4-hydroxy-2 : 6 : 6-trimethylcyclohexane-1-carboxylic acid is a colourless, viscous oil and boils at 176—178° under 8 mm. pressure. The *cis-acid* forms glistening prisms and melts at 141—143°; when heated with potassium hydrogen sulphate, it

j f 2

forms a *lactone* crystallising in leaflets, melting at 56—57°, and boiling at 122—123° under 9 mm. pressure. The *trans-acid* forms glistening, cubical crystals and melts at 151—153°; heating with potassium hydrogen sulphate converts it into trimethylcyclohexenecarboxylic acid. The *ethyl* ester, $\text{OH}\cdot\text{C}_9\text{H}_{16}\cdot\text{CO}_2\text{Et}$, prepared from the mixed acids, is a viscous oil boiling at 150—154° under 17 mm. pressure. It may be oxidised to *ethyl* 2 : 6 : 6-trimethylcyclohexane-4-one-1-carboxylate, a mobile oil boiling at 132—133° under 12 mm. pressure.

4-Hydroxy-2 : 6 : 6-trimethylcyclohexane-1-carbinol,



is a viscous oil boiling at 150—155° under 7—8 mm. pressure, and consists of two isomerides, one of which separates from benzene in colourless crystals, melts at 92—93°, and boils at 152° under 8 mm. pressure.

2 : 6 : 6-Trimethylcyclo- Δ^2 -hexene-4-one-1-carboxylic acid, prepared by saponification of the ester, forms crystals and decomposes into isophorone and carbon dioxide on heating. Several methods of reduction are described.

The cyclohexenecarboxylic acids obtained as by-products in the above preparations are best prepared by heating the hydroxy-acids with phosphoric oxide or trichloride, or potassium hydrogen sulphate. 2 : 6 : 6-Dimethylcyclo- Δ^4 -hexene-1-carboxylic acid is an oil, solidifying on cooling. The *ethyl* ester is a colourless oil with a fragrant odour, and boils at 89—91° under 12 mm. pressure.

Ethyl 2 : 6 : 6-trimethylcyclo- Δ^4 -hexene-1-carboxylate, prepared by heating ethyl trimethylhydroxycyclohexanecarboxylate with phosphorus trichloride and quinoline and heating the phosphorous ester first formed under reduced pressure, boils at 95—98° under 13 mm. pressure. The *acid* boils at 140—142° under 15 mm. pressure, and slowly solidifies to colourless crystals on cooling; it is isomeric with α - and β -cyclogeranic acids.

C. H. D.

Attempts to Synthesise cycloOctane Derivatives. EDUARD BUCHNER AND KURT SCHEDA (*Ber.*, 1904, 37, 931—938).—*Ethyl* Δ^1 -cycloheptenecarboxylate, prepared from the corresponding acid (Braren and Buchner, *Abstr.*, 1900, i, 292; 1901, 85, 385) by heating with alcohol and sulphuric acid, is a colourless oil boiling at 108° under 14 mm. pressure. It reacts with ethyl diazoacetate when heated at 140°, yielding a mixture of esters boiling at 120—175° under 13·5 mm. pressure (the main product distilling at 167°), which is hydrolysed into a mixture of two isomeric acids, $\text{C}_{10}\text{H}_{14}\text{O}_4$. The one crystallises from 100 parts of boiling water in long, colourless needles, melts at 231°, and is not oxidised by permanganate. It contains two carboxylic groups, and forms sparingly soluble *barium*, *calcium*, *lead*, and *silver* salts, but no *anhydride*. The other crystallises from three parts of boiling water in colourless needles, aggregated in clusters, and melts at 132°. It is stable towards permanganate and does not form an anhydride.

Ethyl cycloheptanepyrazolinecarboxylate is obtained as an oil by the interaction of diazomethane and ethyl cycloheptenecarboxylate. It

forms a crystalline *hydrochloride*, $C_8H_{13}N_2 \cdot CO_2Et, HCl$, which melts and partly decomposes at 150° . It was not found possible to eliminate nitrogen from this compound and so obtain a *cyclooctane* derivative.

E. F. A.

Preparation of Methylenehippuric Acid. CHEMISCHE FABRIK AUF AKTIEN, VORM. E. SCHERING (D.R.-P. 148669).—Aldehydes usually condense with the methylene group of hippuric acid; formaldehyde, however, reacts abnormally.

Methylenehippuric acid, $COPh \cdot N < \begin{matrix} CH_2 \cdot CO \\ CH_2 \cdot O \end{matrix}$, prepared by mixing

hippuric acid and paraformaldehyde in sulphuric acid solution, or less conveniently by heating the acid with formaldehyde solution and pouring on to ice after 4 days, crystallises from ethyl acetate in large prisms and melts at 151° . It dissolves sparingly in water, more readily in hot benzene or light petroleum.

C. H. D.

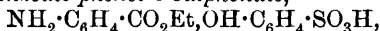
Soluble, Crystalline Derivatives of Aminocarboxylic Esters. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 147580. Compare following abstract).—The phenolsulphonates of aromatic aminocarboxylic esters are readily decomposed by water, and heating for the purpose of sterilisation is therefore impossible. Stable salts, which may be heated alone or with water to 100° without decomposition, are obtained from acids containing a sulpho-group in the side-chain.

Ethyl p-aminobenzoate benzylsulphonate, from ethyl *p-aminobenzoate* hydrochloride and sodium benzylsulphonate, forms white leaflets and decomposes above 235° . *Methyl m-amino-p-hydroxybenzoate benzylsulphonate* forms long, flat needles and melts and decomposes at 235° . *Methyl p-amino-m-hydroxybenzoate benzylsulphonate* forms needles and melts and decomposes at 210° .

C. H. D.

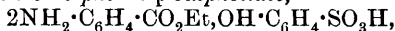
Compounds of Aromatic Aminocarboxylic Esters with Phenolsulphonic Acids. EDUARD RITSERT (D.R.-P. 147790).—Aromatic aminocarboxylic esters are employed as local anaesthetics, but have the disadvantage of insolubility in water, and their soluble salts with inorganic acids are inapplicable on account of their irritant action. Suitable compounds are obtained from phenolsulphonic acids.

Ethyl p-aminobenzoate phenol-o-sulphonate,



prepared by mixing warm solutions of sodium phenol-*o*-sulphonate and ethyl-*p*-aminobenzoate hydrochloride, crystallises from alcohol in needles, melts at 201 – 203° , and is soluble in acetone, insoluble in ether or benzene.

Ethyl p-aminobenzoate phenol-p-sulphonate,



forms very large prisms and melts at 158 – 159° . The normal salt is obtained on boiling with rather more than 1 mol. of free phenol-*p*-sulphonic acid, and crystallises from a mixture of ether and alcohol in tablets melting at 196 – 198° . *Methyl p-aminobenzoate p-cresol-m-sulphonate* is a normal salt, crystallising in slightly red leaflets; it

melts and decomposes at 216—217°. *Ethyl p-aminobenzoate phenol- α -disulphonate* (normal salt) forms slightly yellow, clear crystals, and melts at 220—221°. Water decomposes it partially even in the cold, giving rise to a solution containing about one-third of the total amount of the aminocarboxylate in the free state.

C. H. D.

Sulphamic Acids of Aromatic Carboxylic Esters. HUGO WEIL (D.R.-P. 147552)—Whilst nitrated aromatic carboxylic acids usually react with sulphites to form sulpho-derivatives of amino-acids, their esters react with alkali hydrogen sulphites to form salts of sulphamic acids of the carboxylic esters, according to the equation: $\text{NO}_2 \cdot \text{Ar} \cdot \text{CO}_2\text{X} + 3\text{NaHSO}_3 = \text{CO}_2\text{X} \cdot \text{Ar} \cdot \text{NH} \cdot \text{SO}_3\text{Na} + 2\text{NaHSO}_4$. If these proportions are used, the sodium hydrogen sulphate produced gives rise to the formation of some amino-carboxylic ester; this may be avoided by the addition of a larger quantity of normal sulphite or hydrogen sulphite. Normal sulphites and acetic acid, or the sulphites of alkali earths, zinc, manganese, &c., or sulphur dioxide and an organic base, may also be employed.

The sodium salts of the sulphamic-carboxylic esters crystallise well from 95 per cent. alcohol. They are not decomposed by cold dilute acids, but heating removes the sulpho-group. Cold sodium hydroxide saponifies the esters.

Sodium methyl o-sulphamobenzoate, $\text{CO}_2\text{Me} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{SO}_3\text{Na}$, from methyl *o*-nitrobenzoate, crystallises in large groups of needles and melts at 168° (uncorr.); the corresponding *ethyl* ester is a fine crystalline powder and sinters at 90°, melting and decomposing at 110°. *Sodium methyl m-sulphamobenzoate* forms rhomboidal crystals and sinters at 121°, melting at 171—172°; the *ethyl* ester forms globular aggregates and melts at 115—116°. *Sodium methyl p-sulphamobenzoate* forms slender needles, often twinned, and sinters at 85°, becoming solid on further heating; the *ethyl* ester forms groups of needles, sinters at 55°, then melts and decomposes at 100°, afterwards solidifying. The *ortho*- and *para*-, but not the *meta*-salts, decompose on the water-bath.

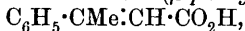
C. H. D.

[Derivatives of Diphenylamine.] KALLE & Co. (D.R.-P. 148341 and 148342).—*Nitroaminohydroxydiphenylaminicarboxylic acid*, prepared by reducing dinitrohydroxydiphenylaminicarboxylic acid (D.R.-P. 108872), crystallises in small, yellow needles and decomposes on melting; it is insoluble in water, readily soluble in alcohol. The *sodium* salt crystallises in metallic, glistening leaflets. Carbon disulphide converts it into the *thiocarbamidicarboxylic acid*, forming small, yellow crystals, insoluble in water. Fusion with sulphur and alkali sulphide forms a blue dye, insoluble in water, but dissolving in alkali sulphides, and becoming reduced to the leuco-compound on warming.

The *aminothiocarbamide* prepared by the action of carbon disulphide on 2:4-diamino-4'-hydroxydiphenylamine is insoluble in water, but dissolves readily in organic solvents, acids or alkalis, and yields a diazo-compound with nitrous acid.

C. H. D.

β -Methylcinnamic Acid. GEORG SCHROETER (*Ber.*, 1904, 37, 1090—1093).— *β -Methylcinnamic acid* (*β -phenylcrotonic acid*),



prepared by condensing acetophenone with ethyl iodoacetate by means of magnesium and hydrolysing the ester which was formed as an intermediate product and was only partially purified, melts constantly at $97-98.8^\circ$, distils completely at $166-168^\circ$ under 11 mm. pressure, is sparingly soluble in water and in cold carbon disulphide, but readily in alcohol, ether, and chloroform, combines with bromine, decolorises permanganate, and forms insoluble silver, lead, copper, and mercury salts; the silver salt was analysed. T. M. L.

Additive Reactions in Compounds with Conjugated Carbon Linkings. F. WILLY HINRICHSSEN (*Ber.*, 1904, 37, 1121—1125. Compare Thiele, *Abstr.*, 1899, i, 554).—Michael and Leighton's results (this vol., i, 242) are confirmed.

[With M. REIMER].—*p*-Nitrophenylcinnamylacrylic acid, obtained from sodium *p*-nitrophenylacetate, acetic anhydride, and cinnamaldehyde, crystallises from alcohol in small, yellow needles melting at 259° . The sodium salt contains $2\text{H}_2\text{O}$. When brominated in moist chloroform solution, a bromo-lactone melting at $169-171^\circ$ is obtained. In carbon disulphide solution, a dibromide, $\text{C}_{17}\text{H}_{13}\text{O}_4\text{NBr}_2$, melting at $207-209^\circ$, is formed.

[With W. TRIEPEL].—Ethyl cinnamylidenemalonate dibromide melts at 93° , and on oxidation yields cinnamic acid dibromide, thus indicating the formula $\text{CHPhBr}\cdot\text{CHBr}\cdot\text{CH}\cdot\text{C}(\text{CO}_2\text{Et})_2$, for the original dibromide.

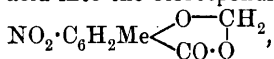
J. J. S.

Pseudonitrosites. A Correction. HEINRICH WIELAND (*Annalen*, 1903, 329, 340).—A question of priority (compare this vol., i, 54, and Angeli, *Abstr.*, 1900, ii, 722; 1902, ii, 254). K. J. P. O.

Action of Formaldehyde on *p*-Nitrophenols. WALTHER BORSCHKE and A. D. BERKHOUT (*Annalen*, 1903, 330, 82—107).—In the action of formaldehyde on phenols, the *p*-hydrogen atom is replaced, or if the para-position is already occupied, an *o*-hydrogen atom, in which case a xanthen derivative is often produced. *p*-Nitrophenols behave in a peculiar manner, 2 mols. of the aldehyde reacting with one mol. of the phenol, a methylene ether being formed; thus, from *p*-nitrophenol, the compound $\text{NO}_2\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{O}-\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \quad \text{O} \end{smallmatrix}$ is obtained (compare *Abstr.*, 1902, i, 836; where this substance was erroneously described as a xanthen derivative). 5-Nitrosalegeninmethylene ether is prepared by adding dilute sulphuric acid to a solution of *p*-nitrophenol in 40 per cent. formaldehyde, when much heat is developed, and a mass of crystals separates; the ether crystallises in needles melting at 148° and can be sublimed; by permanganate, it is oxidised to 5-nitrosalicylic acid. When oxidised by chromic acid in acetic acid solution, the methylene ether ester, $\text{NO}_2\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{O}-\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CO}\cdot\text{O} \end{smallmatrix}$, is obtained, crystallising in pale

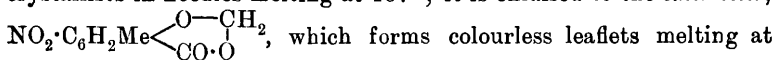
yellow needles or leaflets melting at 110° , and is converted by alkalis into formaldehyde and 5-nitro-2-hydroxybenzoic acid (m. p. 228°).

5-Nitro-*m*-cresol, prepared by oxidising 5-nitroso-*m*-cresol with potassium ferricyanide, yields a *benzoyl* derivative, crystallises in needles melting at 128° ; with formaldehyde, it yields a *methylene ether*, $\text{C}_9\text{H}_9\text{O}_4\text{N}$, which crystallises in colourless needles melting at 133° , and is oxidised by chromic acid into the corresponding *ether ester*,



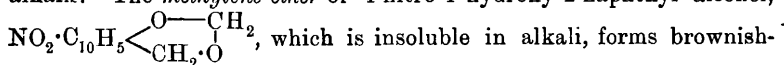
crystallising in needles melting at 143° ; it is converted by alkalis into nitrocresotic acid (m. p. 199°).

Both 4- and 6-nitro-*m*-cresols are formed in the nitration of *m*-cresol; the *benzoate* of the former forms flattened needles melting at 76° , and the *benzoate* of the latter long, pale yellow needles melting at 75° . Formaldehyde yields with 6-nitro-*m*-cresol a *methylene ether* which crystallises in needles melting at 137° ; it is oxidised to the *ether ester*,

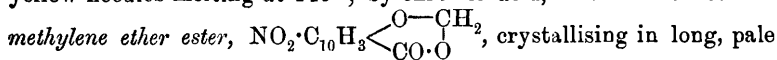


which forms colourless leaflets melting at 96° . On hydrolysis, it is converted into 6-nitro-3-hydroxy-2-cresotic acid, which crystallises in yellow needles melting at 219° , and was obtained by nitrating 4-methylsalicylic acid.

4-Nitro-*a*-naphthol and formaldehyde yield two substances which can be separated by taking advantage of the fact that one is soluble in alkalis. The *methylene ether* of 4-nitro-1-hydroxy-2-naphthyl alcohol,



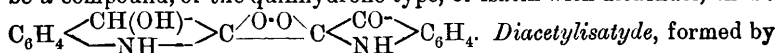
yellow needles melting at 149° ; by chromic acid, it is oxidised to the



yellow needles melting at $167-168^{\circ}$; by alkalis, it is hydrolysed, formaldehyde and 4-nitro-1-hydroxy-2-naphthoic acid (m. p. 212°) being formed. The substance, which is soluble in alkali, is 1:1'-*dinitro-4:4'-dihydroxydinaphthylmethane*, which forms lemon-yellow needles melting and decomposing at about 200° . It is oxidised by chromic acid to the corresponding *dinaphthyl ketone*, $\text{CO}[\text{C}_7\text{H}_5(\text{OH})\cdot\text{NO}_2]_2$, which is a reddish-brown, amorphous substance, melting and decomposing at 130° .

Formaldehyde and 6-nitroresorcinol (the *dibenzoate* of which crystallises in brownish-yellow needles melting at 109°) yield very small quantities of a substance, $\text{C}_8\text{H}_7\text{O}_5\text{N}$, which crystallises in needles melting at 130° . K. J. P. O.

Reduction of Isatin. GUSTAV HELLER (*Ber.*, 1904, 37, 938-950).—Isatyde, $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_4$, obtained by the reduction of isatin, is shown to be a compound, of the quinhydrone type, of isatin with dioxindol, thus:



reducing acetylisyatin, crystallises in small nodules, which sinter at 195° and melt and decompose at 198° ; the corresponding *dibenzoylisyatyde* melts at 186° . Dioxindole sinters at 160° and melts to a colour-

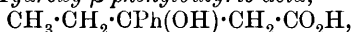
less mass at 170° ; it forms a crystalline *hydrochloride*, which is stable when dry and melts at 156° . *Benzoyldioxindole* crystallises in needles from light petroleum or in prisms from alcohol, and melts at 134° . *Dibenzoyldioxindole*, formed on benzoylating indole in presence of an alkali hydroxide, crystallises from alcohol in needles and melts at 170° . When heated with phenylhydrazine, dioxindole forms isatine-phenylhydrazone.

[With KARL AMBERGER.]—The *nitrile* of *o*-nitromandelic acid, prepared by treating *o*-nitrobenzaldehyde with aqueous sodium hydrogen sulphite and adding potassium cyanide to the product, crystallises from benzene in long needles melting at 95° ; hydrogen chloride converts this into the *hydrochloride* of *o*-nitrophenyloxyacetimidooethyl ether, which melts and decomposes at 133° .

Ethyl o-nitromandelate crystallises in long, colourless needles aggregated in clusters, which melt at 49 – 50° . When reduced with zinc dust and acetic acid, *o*-nitromandelic acid forms dioxindole, the synthetical substance being in every way identical with that prepared from isatin.

E. F. A.

β -Phenyl- β -ethyl-lactic Acid [**β -Hydroxy- β -phenylbutyric Acid**]. PAUL MICHNOVITSCH (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 1188–1192).— **β -Hydroxy- β -phenylbutyric acid**,



prepared by oxidising phenylethylallylcarbinol by means of potassium permanganate, separates from ether in rhombic plates or prisms which melt at 118 – 121° , and are readily soluble in water. Its *barium*, *calcium*, and *silver* salts were prepared and analysed.

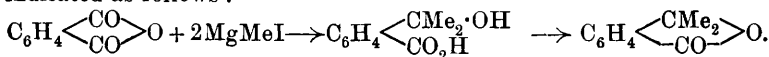
T. H. P.

New Preparation of *o*-Phenoxybenzoic Acid (Salicylic Acid Phenyl Ether). FRITZ ULLMANN (*Ber.*, 1904, 37, 853–854).—Salicylic acid phenyl ether is conveniently prepared by adding a small quantity of finely-divided copper to a hot solution of potassium *o*-chlorobenzoate in phenol, potassium chloride immediately separating.

[With A. LEHNER.]—*o*-Chlorobenzoic acid and benzenesulphinic acid condense in presence of copper, forming diphenylsulphone-*o*-carboxylic acid. A number of similar condensations are now being studied.

C. H. D.

Preparation of Dialkylphthalides. HUGO BAUER (*Ber.*, 1904, 37, 735–737).—The methods hitherto in use for preparing dialkylphthalides give very poor yields; that now described, which consists in the action of magnesium alkyl iodides on phthalic anhydride, gives a yield 70–80 per cent. that of theory. In principle, the action is similar to that of magnesium alkyl iodides on acetic and benzoic anhydrides (compare Tissier and Grignard, *Abstr.*, 1901, i, 316), and is indicated as follows:



Dimethylphthalide melts at 67 – 68° , boils at 274 – 275° (Kothe gives 271° , *Abstr.*, 1889, 257), and with nitric acid gives a *mononitro*-derivative, which crystallises from light petroleum in slender, felted

needles melting at 131—132°. Diethylphthalide, as stated by Rjasantzeff (Abstr., 1889, 1059), melts at 54° and gives a *nitro*-derivative crystallising in yellow needles and melting at 103—104°.

W. A. D.

Preparation of Nitro-derivatives of Aromatic Amines from Phthalimides. RUDOLF LESSER (D.R.-P. 148874. Compare Abstr. 1903, i, 618).—Nitrophthalamic acids may be combined with aromatic bases in the same way as nitrophthalimides, the reaction taking place at moderate temperatures, so that heating under pressure is not necessary. Phthalimides are recovered, the phthalamic acids formed at first being very unstable. The nitrophthalamic acids may be prepared from phthalimides by conversion into phthalamic acids and subsequent nitration, or by nitration, and conversion into nitrophthalamic acids by boiling with potassium hydroxide. The substances obtained, for example, in the case of the condensation with aniline, are: phthalanil, nitrophthalanil, and nitrophthalamic acid; the last of these, on boiling with aniline, forms nitroaniline and phthalanil.

C. H. D.

Transformation of Unsaturated Acids. RUDOLF FITTIG (*Annalen*, 1904, 330, 292—361. Compare Abstr., 1899, i, 332, 417).—In this paper, which is a continuation of the previous work (*loc. cit.*) on the intramolecular changes of unsaturated acids, an account is given of all the possible isomerides of phenyl-paraconic and isoparaconic acids (compare Kreutz, Abstr., 1902, i, 462); the four active and the two inactive acids have now been isolated.

Transformation of Methylparaconic into Methylitaconic Acid, and Attempts to obtain Methylatlaticonic Acid.—[With OSCAR SCHEEN.]—The yield of methylparaconic acid has been improved by directly esterifying the crude acid obtained from ethyl acetosuccinate (Abstr., 1895, i, 204); the *ethyl* ester is a colourless liquid of the consistence of glycerol, boiling at 273—273.5°.

Methylitaconic acid was prepared by the action of sodium ethoxide on ethyl methylparaconate, a yield of 30—35 per cent. of the pure acid (m. p. 166—167°) being obtained. A search was made for by-products by esterifying the oily acids and fractionally distilling the product; *ethyl ethoxyethylsuccinate*, $\text{CO}_2\text{Et}\cdot\text{CH}(\text{CHMe}\cdot\text{OEt})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, was obtained as a colourless oil of pleasant smell, boiling at 253—255°; the free *acid* is a colourless, extremely viscid liquid; the *calcium* salt, $\text{C}_8\text{H}_{12}\text{O}_5\text{Ca}$, is more soluble in cold than in hot water, the *barium* salt is very soluble, and the *silver* salt is a white powder. When heated with fuming hydrochloric acid under pressure at 140°, this acid is converted into methylparaconic acid.

All attempts to convert methylitaconic into methylatlaticonic acid by boiling with concentrated sodium hydroxide failed; the major part of the methylitaconic acid was recovered unchanged, a very small amount of methylparaconic acid being alone isolated.

Derivatives of Dimethylatlaticonic Acid.—[With WALTHER FRIEDMANN.]—(Compare Abstr., 1899, i, 335.) In order to prepare *isoheptodilactone* or *hydroxyisoterebic acid* from dimethylatlaticonic acid, it is unnecessary to isolate the *bromoisoterebic acid*; the cold aqueous suspension of the

dimethylaticonic acid is treated with the requisite quantity of bromine, saturated with sodium hydroxide, and kept for 24 hours, when an excellent yield of the dilactone is formed; or, in order to prepare the hydroxyisoterebic acid, the liquid is diluted after bromination and boiled for ten hours, and then extracted with ether.

Owing to the apparent difficulty of opening the lactone ring of hydroxyisoterebic acid on dissolution in an alkali hydroxide (compare *loc. cit.*), it was thought that possibly conversion into the dilactone acid occurred; this was, however, found not to be the case; only pure hydroxyisoterebic acid was recovered from the salts. Similarly, on neutralising the isoheptodilactone, both rings are opened, but no transformation takes place, the pure dilactone being obtained from the salts. When, however, hydroxyisoterebic acid is neutralised at a higher temperature, a small amount of conversion does occur, the dilactone being obtained from the resulting salt. No transformation of the dilactone takes place in similar circumstances. The *barium* salt, $C_7H_{10}O_6Ba$, derived from the dilactone, is a hygroscopic, crystalline powder, whilst that prepared from hydroxyisoterebic acid crystallises with $3\frac{1}{2}H_2O$, $2H_2O$ being lost at 100° . The *barium* salt of the monobasic lactonic acid, $(C_7H_9O_5)_2Ba, 2H_2O$, can be prepared from hydroxyisoterebic acid, isoheptodilactone yielding a similar *barium* salt crystallising with $1H_2O$.

Attempts to convert the dilactone into the hydroxy-acid by the action of concentrated hydrochloric acid, or to convert the hydroxy-acid into the dilactone by heat, failed; it was found, however, that the hydroxyisoterebic acid was slowly changed into the dilactone when its solution in excess of sodium hydroxide was kept for 12 days, in this period, 64 per cent. of the dilactone being formed. Under similar conditions, no reverse change of the dilactone into the hydroxy-acid occurs.

Derivatives of Phenylaticonic Acid.—[With ADOLF BRESLAUER.]—Phenylaticonic acid is to a small extent converted into phenylbromoisoparaconic acid, $C_5H_4O_4PhBr$, when it is acted on by bromine in chloroform solution in diffused daylight, but it is much more readily produced by carrying out the bromination in the presence of water; the acid crystallises in star-shaped clusters of needles melting at 147° , and belonging to the monoclinic system. Although the melting point of the acid only differs by 3° from that of phenylparaconic acid, which is prepared from phenylitaconic acid (Fittig and Leoni, *Abstr.*, 1897, i, 894), the crystalline habit of the two acids is quite distinct. Both acids yield the same benzoylpropionic acid when boiled with water. On reduction with sodium amalgam, phenylbromoisoparaconic acid is converted into a mixture of phenylparaconic acid and phenylisoparaconic acids, the latter being formed in only small quantity; the yield is somewhat increased when the alkalinity is kept as low as possible by addition of sulphuric acid during the reduction. *Phenylisoparaconic acid*, $C_5H_5O_4Ph$, crystallises in leaflets melting at 170° and behaves on neutralisation as a monobasic lactonic acid. The *barium* salt, $(C_{11}H_9O_4)_2Ba$, is a soluble crystalline solid; the *barium* salt, $(C_{11}H_{10}O_5)_2Ba$, of the dibasic hydroxy-acid is crystalline and far less soluble.

Isomeric Phenylparaconic Acids.—[With PAUL JEHL.]—Owing to Fichter and Dreyfus' observation (Abstr., 1900, i, 426) that phenylparaconic acid is partly converted into the isoparaconic acid by boiling with excess of sodium hydroxide for 24 hours, the conditions of transformation of these acids into each other has been investigated. When phenylparaconic acid is boiled with the alkali hydroxide, 22—25 per cent. of phenylitaconic acid, 30—33 per cent. of phenylisoparaconic acid, and 40—46 per cent. of phenylparaconic acid are produced. When phenylisoparaconic acid is similarly treated, 7 per cent. of phenylitaconic, 31 per cent. of phenylisoparaconic, and 61 per cent. of phenylparaconic acids are obtained. When the *iso*-acid is boiled with water, no change occurs, but when heated under pressure with water, a more complicated decomposition was observed, phenylparaconic and phenylisocrotonic acids, and phenylbutyrolactone being formed. If the *iso*-acid is boiled with dilute hydrochloric acid, it is entirely changed, phenylparaconic and phenylisocrotonic acids, and phenylbutyrolactone being formed. On boiling phenylisoparaconic acid with excess of barium hydroxide, no transformation takes place.

When phenylisoparaconic acid is distilled, it yields the same products as phenylparaconic acid, unchanged acid, phenylbutyrolactone, and phenylisocrotonic acid. This behaviour is due to the fact that phenylisoparaconic acid is largely changed on heating into phenylparaconic acid, which then decomposes into phenylisocrotonic acid.

Phenylisoparaconic acid is decomposed into its two active modifications by the aid of its strychnine salts in the same manner as Kreutz (*loc. cit.*) employed for the phenylparaconic acid. From the insoluble strychnine salt, which crystallises in needles and melts at 120—130°, the *d*-acid was obtained, and from the soluble strychnine salt, which crystallises in plates melting at 165—170°, the *l*-acid. Both acids form large crystals melting at 182°; in alcohol, the *d*-acid has $[\alpha]_D + 14.72^\circ$, and the *l*-acid $[\alpha]_D - 14.51^\circ$ at 20°; in acetic acid, the *d*-acid has $[\alpha]_D - 6.95^\circ$, and the *l*-acid $[\alpha]_D + 7.29^\circ$, at 20°. In acetic acid therefore the rotation is reversed. *Penicillium glaucum* also effects a separation of the two forms, destroying the *l*-acid more readily. At a high temperature, each of the acids racemises, but boiling of either acid alone or in the form of its barium salt has no effect. A crystallographic investigation showed that the racemic phenylisoparaconic acid belongs to the monoclinic system [$a:b:c = 2.6842:1:2.1225$, and $\beta = 80^\circ 23'$]; the active acids crystallise in the rhombic system [$a:b:c = 0.9022:1:2.4024$].

Kreutz's work on phenylparaconic acid has been repeated and in numerous points corrected. The strychnine salts of the active acids are separated by crystallisation from absolute alcohol, the salt of the *l*-acid separating first in plates melting at 197—202°, and the salt of the *d*-acid separating afterwards in needles melting at 100—102°. Each acid crystallises with $\frac{1}{2}H_2O$ from aqueous solvents, but from ether or acetone in forms melting at 134°. The *d*-acid has in alcoholic solution $[\alpha]_D + 64.33^\circ$, and the *l*-acid $[\alpha]_D - 65.33^\circ$; in acetic acid solution, the *d*-acid has $[\alpha]_D + 75.91^\circ$, and the *l*-acid $[\alpha]_D - 76.34^\circ$; in all cases, the temperature was 20°. Anhydrous phenylparaconic acid crystallises in monoclinic forms [$a:b:c = 1.3644:1:2.4853$ and

$\beta = 87^{\circ}55'$ melting at 121° ; the active forms crystallise in the rhombic system [$a:b:c = 1.0886:1:x$]. Measurements of the electrical conductivity of the two racemic acids have given the values, for phenylparaconic acid, K 0.000480, and for phenylisoparaconic acid, K 0.000404.

Transformations of Diphenylitaconic Acid.—[With ALFRED RIECHE.]—When boiled with concentrated sodium hydroxide, phenylitaconic acid undergoes no change, but when heated, decomposition occurs. At 170 — 180° under 20 mm. pressure in a slow current of air, benzophenone distils over, and the residue contains diphenylitaconic anhydride, crystallising in pale yellow needles melting and decomposing at 147 — 150° (Stobbe and Kohlmann, Abstr., 1899, i, 900). Diphenylcitraconic anhydride, $\text{CHPh}_2 \cdot \text{C} \begin{smallmatrix} \text{CH} \cdot \text{CO} \\ \text{CO} \cdot \text{O} \end{smallmatrix}$, is formed together with the anhydride last mentioned, and is more soluble in carbon disulphide; it crystallises in colourless prisms and from benzene in plates with 1 mol. of benzene, and melts and decomposes at 96 — 98° . The acid crystallises in needles melting and decomposing at 105 — 115° and very readily passes into the anhydride. The calcium salt crystallises with $2\text{H}_2\text{O}$ in needles, the barium salt with $3\frac{1}{2}\text{H}_2\text{O}$ in prisms, and the silver salt is amorphous. When boiled with 10 per cent. sodium hydroxide or heated with water under pressure at 200° , this acid is completely changed into diphenylitaconic acid. Treatment of the diphenylcitraconic acid with bromine in sunlight did not lead to the formation of diphenylmesaconic acid; the use of dilute nitric acid was equally fruitless. On reduction with sodium amalgam, this acid is converted into diphenylmethylsuccinic acid. K. J. P. O.

Hexahydro-m-tolualdehyde. ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1904, 37, 850—853. Compare Bouveault, this vol., i, 61).—*m*-Bromomethylcyclohexane, prepared by reducing an ethereal solution of *m*-methylcyclohexanone with sodium, saturating with hydrogen bromide, and warming, is optically inactive. It reacts vigorously with magnesium powder, and the product reacts with ethyl orthoformate to form the acetal, which is distilled, the fraction boiling above 120° being hydrolysed by means of 5 per cent. hydrochloric acid. The aldehyde is isolated by decomposing its sodium hydrogen sulphite compound with sodium carbonate. *Hexahydro-m-tolualdehyde*, $\text{C}_6\text{H}_{10}\text{Me} \cdot \text{CHO}$, boils at 176 — 178° under 760 mm., and at 96 — 97° under 50 mm. pressure, a small quantity of a less volatile aldehyde being formed after a time or on heating. It has a sharp, naphtha-like odour, and has a sp. gr. 0.9279 at $0/0^{\circ}$, and 0.9091 at $20^{\circ}/0^{\circ}$. The semicarbazone crystallises from a mixture of alcohol and light petroleum in needles and melts at 158 — 159° , insoluble in water, very soluble in alcohol, acetone, or chloroform, sparingly so in benzene.

In addition to the acetal, small quantities of methylcyclohexene and dimethyldicyclohexyl are obtained. C. H. D.

A General Method of Synthesising Aldehydes. F. BODROUX (*Compt. rend.*, 1904, 138, 700—701).—It has already been shown (this vol., i, 250) that ethyl orthoformate reacts with aromatic organo-

magnesium compounds giving the ethylacetal of an aromatic aldehyde. The yield of the latter is never very good, and diminishes with increase of carbon in the aromatic radicle. It is found that better yields are obtained by operating at higher temperatures. Dry toluene (150 grams for every gram-atom of magnesium) is added to the ethereal solution of the organo-magnesium compound and the excess of ether distilled off. The residue is maintained at 100° and the orthoformate ($\frac{2}{3}$ — $\frac{3}{4}$ mol.) gradually added; after the reaction is over, the acetal can be isolated in the usual manner. The following aldehydes were prepared: phenylacetaldehyde, α -naphthaldehyde, *p*-bromobenzaldehyde, *p*-chlorobenzaldehyde, butaldehyde, and isovaleraldehyde. The yields varied from 55 per cent. in the case of phenylacetaldehyde to 75 per cent. in butaldehyde. S. S.

Action of Methyl Sulphate on Anthranil and *o*-Aminobenzaldehyde. EUGEN BAMBERGER (*Ber.*, 1904, 37, 966—990. Compare Heller, this vol., i, 160).—It is shown that the supposed N-methylantranil, $C_6H_4 \begin{smallmatrix} \text{NM}e \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix}$, described by Heller, which differed very considerably

in its properties from Bamberger's *C*-methylantranil, $C_6H_4 \begin{smallmatrix} \text{N} \\ | \\ \text{C} \text{Me} \end{smallmatrix} \text{O}$,

as also from anthranil itself, is, in reality, a mixture of *o*-dimethylaminobenzaldehyde, *o*-methylaminobenzaldehyde, and a small quantity of *o*-aminobenzaldehyde. *o*-Dimethylaminobenzaldehyde, $NMe_2 \cdot C_6H_4 \cdot CHO$, which is formed in quantity by the action of methyl sulphate on anthranil in the cold, is a light yellow oil boiling at 120° under 11 mm. pressure. The following derivatives have been characterised: the golden-yellow, crystalline *mercurichloride* melts between 90° and 95° to a syrup, and on further heating becomes brown at 135°; the *platinichloride* forms needles, which melt and decompose at 205—206°; the *aurichloride* softens at 121° and melts at 124—125°; the *stannichloride* crystallises in colourless needles or glistening prisms from hydrochloric acid, which melt and decompose at 226—230°. The *sulphite* forms colourless, glistening needles or prisms and melts and decomposes at 162°; the *p*-nitro-*phenylhydrazone* crystallises from alcohol in compact, glistening, reddish-purple prisms with a metallic lustre, melts at 190·5—191°, and forms a *hydrochloride*, which crystallises in orange-yellow, silky, glistening needles. The *phenylhydrazone* crystallises from dilute hydrochloric acid in straw-yellow needles melting at 74—74·5°. *o*-Dimethylaminobenzaldoxime, $NMe_2 \cdot C_6H_4 \cdot CH:N \cdot OH$, forms colourless, silky, glistening needles melting at 87—87·2°. *o*-Aldehydophenyltrimethylammonium iodide, $(CHO \cdot C_6H_4 \cdot NMe_3)I$, prepared by combining the aldehyde with methyl iodide, crystallises from alcohol in colourless, nacreous, glistening plates resembling naphthalene, which melt and decompose at 163·5°.

o-Methylaminobenzaldehyde, $NHMe \cdot C_6H_4 \cdot CHO$, is also formed when methyl sulphate acts on anthranil, and is obtained in quantity by slightly modifying the conditions. The following derivatives have been prepared to characterise it: the *mercurichloride* forms golden-yellow, glistening needles, which soften at 105° and melt to a black liquid at 141—142°; the yellow needles of the *platinichloride* melt at

200—201°; the *aurichloride* is obtained as a light yellow, crystalline product, which rapidly darkens; the *stannichloride* forms colourless, glistening prisms, which melt at 208—209°. *Benzoylmethylaminobenzaldehyde*, $\text{NMeBz} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$, crystallises in white, glistening needles melting at 78·5—79°; the *phenylhydrazine* forms pale yellow, almost colourless, silky needles melting at 124·5—125·5°; the *p-nitrophenylhydrazine* crystallises in deep bordeaux-red, glistening needles with a greenish-gold lustre, and melts at 245—246°.

The *oxime* forms snow-white, silky needles melting at 50·5—51°; *anhydromethylaminobenzaldehyde*, $\text{C}_{16}\text{H}_{16}\text{ON}_2$, crystallises from light petroleum in strongly refractive, colourless, glistening prisms melting at 139·5—140°.

The *o*-mono- and *o*-di-methylaminobenzaldehydes prepared directly by methylation of aminobenzaldehyde with methyl sulphate were in every way identical with the compounds formed from anthranil.

E. F. A.

Preparation of *p*-Alkylaminobenzaldehydes. FRITZ ULLMANN and BURKHARD FREY (*Ber.*, 1904, 37, 855—866).—Alkylated anilines combine with formaldehyde in presence of hydrochloric acid to form alkylaminobenzyl alcohols. Nitrosodimethylaniline oxidises these to the corresponding aldehydes, together with the anhydro-base. This method may be used for the preparation of alkylaminobenzaldehydes.

Ethylaniline, formaldehyde, *p*-nitrosodimethylaniline, and hydrochloric acid react together on warming. The product is best converted, by addition of sulphanilic acid, into *p*-ethylaminobenzylidenesulphanilic acid, which forms a reddish-brown, insoluble, crystalline powder. Alkalis decompose it, forming *p*-ethylaminobenzaldehyde, which crystallises in colourless needles, melts at 79°, dissolves readily in alcohol, ether, benzene, hot water, or boiling light petroleum. The *phenylhydrazine* forms yellow needles, dissolving readily in benzene or glacial acetic acid, sparingly in hot alcohol, and melts at 178°; the *oxime* melts at 118° and dissolves readily in alcohol, benzene, or sodium hydroxide.

p-Dimethylaminobenzaldehyde (Bössneck, *Abstr.*, 1886, 874) may be prepared from *p*-dimethylaminobenzylideneaminodimethylaniline (Mohlau and Fritzsche, *Abstr.*, 1893, i, 470) by the action of either nitrous acid or formaldehyde. The *phenylhydrazine* crystallises in yellow needles and melts at 148°.

p-Diethylaminobenzylidenephénylhydrazine forms large, yellowish-brown needles and melts at 103°; the *oxime* melts at 93°.

The condensation-product from methylethylaniline is *p*-methylethylaminobenzylidene-*p*-aminodimethylaniline, crystallising from benzene in slender, yellow needles and melting at 216°, dissolving readily in benzene, sparingly in hot alcohol. Boiling with formaldehyde and acetic acid forms *p*-methylethylaminobenzaldehyde, which melts at 14° and boils at 180° under 20 mm. pressure. The *phenylhydrazine* forms brownish-yellow needles and melts at 114°.

Methyl-*o*-toluidine, formaldehyde, hydrochloric acid, and nitrosodimethylaniline form *p*-methylamino-*m*-methylbenzylidene-*p*-dimethyl-

aminoaniline, $\text{NHMe} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CH} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$, which crystallises from alcohol in small, yellowish-green prisms, melts at 162° , and dissolves readily in benzene or hot alcohol. Acetic acid and formaldehyde decompose it, forming *6-methylamino-3-tolualdehyde*, which forms slender, almost colourless, glistening needles, melts at 115° , and crystallises from boiling water in leaflets. The *phenylhydrazone* forms yellow needles and melts at 124° . *6-Ethylamino-3-tolualdehyde*, prepared in similar manner, crystallises in slightly yellow, glistening prisms and melts at 69.5° . The *phenylhydrazone* forms yellow needles and melts at 95° ; the *oxime* forms colourless leaflets and melts at 82° .

2-Chloro-4-dimethylaminobenzaldehyde, from *m*-chlorodimethylaniline, crystallises from light petroleum in almost colourless needles and melts at 82° ; the *phenylhydrazone* forms yellow needles and melts at 122° . Nitric and sulphuric acids form *2-chloro-5-nitro-4-dimethylaminobenzaldehyde*, which forms large, yellow prisms and melts at 125° ; the *phenylhydrazone* crystallises in reddish-violet needles, melts at 166° , and dissolves in hot benzene or acetic acid to orange solutions. The *oxime* forms orange needles and melts at 178° . *Chloronitrodimethylaminobenzylideneaniline* crystallises in brick-red needles and melts at 118° . The aldehyde also condenses with benzenesulphonic acid, forming *4-nitrodimethylaminodiphenylsulphone-2-aldehyde* (compare Abstr., 1901, i, 383), which forms yellow leaflets melting at 96° . C. H. D.

Nitro-p-dimethylaminobenzaldehyde. EMILIO NOELTING and JULES DEMANT (*Ber.*, 1904, 37, 1028—1032).—On oxidising 3-nitro-4-dimethylaminobenzaldehyde with alkaline potassium permanganate, *3-nitro-4-methylaminobenzoic acid*, $\text{NHMe} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{CO}_2\text{H}$, is obtained, not the corresponding dimethylaminobenzoic acid; it crystallises from alcohol in yellow needles, melts at 288° , and on acetylation gives the *acetyl* derivative, $\text{NMeAc} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{CO}_2\text{H}$, which forms yellow needles and melts at 190° ; the *ethyl* ester, $\text{NHMe} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{CO}_2\text{Et}$, crystallises from alcohol and melts at 101 — 102° .

3-Nitro-4-dimethylaminobenzaldoxime, prepared from the aldehyde and hydroxylamine, crystallises from alcohol in large, orange-coloured prisms melting at 132° and, when heated with acetic anhydride and sodium acetate, is converted into *3-nitro-4-dimethylaminobenzonitrile*, which forms four-sided, yellow leaflets and melts at 114 — 115° . *3-Nitro-4-dimethylaminobenzoic acid*, obtained by hydrolysing the nitrile with alcoholic sodium hydroxide, forms bright yellow needles, melts at 214 — 215° , and gives an *ethyl* ester, crystallising in leaflets, and melting at 80 — 81° ; the same acid is obtained by directly nitrating *p*-dimethylaminobenzoic acid. On oxidising 3-nitro-4-dimethylaminobenzoic acid with alkaline potassium permanganate, the foregoing 3-nitro-4-methylaminobenzoic acid is formed. W. A. D.

Terpenes and Ethereal Oils. Transformation of 1:3- into 1:2-Methylcyclohexanone. OTTO WALLACH [with ULRICH FRANKE] (*Annalen*, 1903, 329, 368—380).—In order to study further the transformation of one cyclic hexanone into an isomeride (Abstr., 1902, i, 806), the transformation of 1-methyl-3-cyclohexanone into 1-methyl-

2-cyclohexanone has been effected. 1-Methylcyclohexanone was obtained from a tetrahydrotoluene, an account of which has previously been given (Abstr., 1902, i, 750). The nitrosate of tetrahydrotoluene crystallises in needles melting at 107—108°. When the hydrocarbon is oxidised at 0° by one per cent. permanganate, δ -acetylvaleric acid is obtained, and can be isolated as the semicarbazone (m. p. 144—146°); the hydrocarbon must therefore be represented by the formula $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 - \text{CH} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CMe}$, and is probably identical with the hydrocarbon (b. p. 108°) obtained by Markownikoff (Abstr., 1900, i, 579) and called "a-naphthylene."

When the nitrosate is warmed with sodium methoxide, an *oxime* is obtained, which forms crystals melting at 40—42°, and boils at 115—117° under 11 mm. pressure (compare *loc. cit.*). It yields two benzoyl derivatives, an α -compound, which crystallises in needles melting at 142—143°, and is sparingly soluble in ether, and a β -compound melting at 90—91° and readily soluble in ether. On boiling the *oxime* with hydroxylamine hydrochloride, it undergoes an isomeric change into an *oxime* which melts at 62—63°, and yields a benzoyl derivative melting at 142—143°. By warming with sulphuric acid, both *oximes* are converted into methylcyclohexenone, the sp. gr. of which is now given as 0.9680, and the n_D as 1.4831 at 20° (compare *loc. cit.*). The semicarbazone melts at 207—208°.

1:2-Methylcyclohexanol, $\text{C}_7\text{H}_{13}\cdot\text{OH}$, prepared by reducing the methylcyclohexenone by sodium and alcohol (Abstr., 1902, i, 801), boils at 168—170° and has a sp. gr. 0.921 and n_D 1.4696; the phenylurethane obtained from it melts at 103—104°.

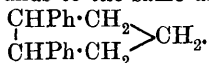
The methylcyclohexanol is oxidised by chromic acid to 1:2-methylcyclohexanone, which was found to be identical with the compound synthesised from methyladipic acid by Zelinsky and Generosoff (Abstr., 1896, i, 350); it has n_D 1.4461 at 21.5°, and forms an *oxime* melting at 43—44°, the benzoyl derivative of which melts at 70—72°. When oxidised by chromic acid in the presence of dilute sulphuric acid, δ -acetylvaleric acid is formed; its constitution was fixed by oxidising it to adipic acid by means of sodium hypobromite. K. J. P. O.

Preparation of ψ -Ionone. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 147839).—In the preparation of ψ -ionone by the condensation of citral with acetone, the yield is considerably improved when the reaction is carried out in the absence of water. Sodamide or potassamide is employed as a condensing agent, and benzene is added, if necessary, to dilute the reacting substances. C. H. D.

Action of Phosphorus Pentasulphide on Benzophenone-oxime. R. CIUSA (*Gazzetta*, 1904, 34, i, 102—104).—Phosphorus pentasulphide reacts explosively with benzophenoneoxime at 80°; in boiling carbon disulphide solution, the action takes place smoothly, a substance, $\text{C}_{10}\text{H}_{10}\text{O}_3\text{S}$, being formed, which crystallises from aqueous alcohol in plates, melts at 86°, and, on reduction with zinc and hydrochloric acid, evolves hydrogen sulphide. W. A. D.

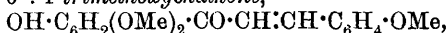
Conversion of Dibenzylideneacetone into Derivatives of Diphenylcyclopentane. DANIEL VORLANDER and HEINRICH VON LIEBIG (*Ber.*, 1904, **37**, 1133—1134).—The compound, $C_{17}H_{14}O_2$, obtained by Vorlander and Schrödter (*Abstr.*, 1903, i, 496) by the action of acetic anhydride and sulphuric acid on dibenzylideneacetone may be regarded as a derivative of *cyclopentane*, the β -carbon atoms having become linked together. This view is confirmed by the oxidation of the compound to benzil and desylacetic acid by chromic acid or potassium permanganate. It is therefore a keto-enolic compound having the formula $\begin{array}{c} \text{CHPh}\cdot\text{CH}_2 \\ | \\ \text{CPh}:\text{C}(\text{OH}) \end{array} > \text{CO}$, and is isomeric with anhydroacetone-

benzil, $\begin{array}{c} \text{OH}\cdot\text{CPh}\cdot\text{CH}_2 \\ | \\ \text{CPh}=\text{CH} \end{array} > \text{CO}$ (Japp, Burton, and Lander, *Trans.*, 1887, **51**, 420; *Proc.*, 1896, 108), which has no acid properties. Hydriodic acid reduces both compounds to the same diphenylcyclopentane,



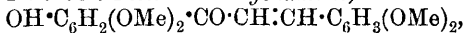
The hydrocarbon, $C_{15}H_{14}$, obtained by the action of concentrated potassium hydroxide on the keto-enolic compound and described as an α -methylstilbene, is identical with the α -methylstilbene prepared by Klages (*Abstr.*, 1902, i, 668) from deoxybenzoin and magnesium methyl iodide, and by Hell (*this vol.*, i, 242) from acetophenone and magnesium benzyl chloride, although the melting points of the hydrocarbon and its dibromide show slight differences. C. H. D.

Synthesis of Yellow Vegetable Dyes. STANISLAUS VON KOSTANECKI and JOSEF TAMBOR (*Ber.*, 1904, **37**, 792—794).—*2'-Hydroxy-4' : 6' : 4-trimethoxychalkone*,



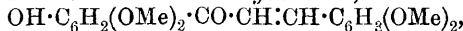
prepared from phloracetophenone dimethyl ether and anisaldehyde, crystallises from alcohol in yellow needles and melts at 113° . The *acetyl* derivative, $C_{26}H_{20}O_6$, crystallises from alcohol in pale yellow flakes and melts at 120° .

2'-Hydroxy-4' : 6' : 3 : 4-tetramethoxychalkone,



prepared from phloracetophenone dimethyl ether and veratraldehyde, crystallises from alcohol in yellow flakes and melts at 157° . The *acetyl* derivative, $C_{21}H_{20}O_7$, crystallises from dilute alcohol in pale yellow needles and melts at 107° .

2'-Hydroxy-4' : 6' : 2 : 4-tetramethoxychalkone,



prepared from phloracetophenone dimethyl ether and 2 : 4-dimethoxybenzaldehyde, crystallises from a mixture of benzene and light petroleum or from alcohol in deep yellow needles and melts at 152° . The *acetyl* derivative, $C_{21}H_{20}O_7$, crystallises from alcohol in bright yellow needles and melts at 118 — 119° .

It is proposed, by applying the methods described later (*this vol.*, i, 440, 441), to synthesise from this series of *o*-hydroxychalkones the natural dyes galangin, kaempferol, quercetin, and morin. T. M. L.

Reactions of Unsaturated Ketones. CARL D. HARRIES (*Annalen*, 1904, 330, 185—279).—In the long introduction to this paper, a very detailed account is given of our present knowledge of the properties of unsaturated ketones; the nature of the ethylene linking is also discussed, and two or three instances of addition to a conjugated pair of ethylene linkings are quoted, which are not in agreement with Thiele's hypothesis of partial valence.

I. Aromatic $\alpha\beta$ -Unsaturated Ketones.—[With FRIEDRICH GOLLNITZ].—*Dypnonehydroxylamine*, $\text{CMePh}(\text{NH}\cdot\text{OH})\cdot\text{CH}_2\cdot\text{COPh}$, is formed whenever dypnone and hydroxylamine are kept together in alcoholic solution for several days; it forms a colourless, crystalline substance melting at $109\text{--}110^\circ$, reduces Fehling's solution, and is oxidised to an unstable, blue nitroso-compound; its *acid oxalate*, $\text{C}_{18}\text{H}_{19}\text{O}_6\text{N}$, melts at 63° ; with phenylcarbimide, it yields a *carbamide*, $\text{C}_{23}\text{H}_{22}\text{O}_3\text{N}_2$, which is a microcrystalline powder melting at 127° , and with phenylhydrazine a *phenylhydrazone*, $\text{C}_{22}\text{H}_{23}\text{ON}_3$, which is a microcrystalline substance melting at $125\text{--}126^\circ$. In the formation of dypnonehydroxylamine, a by-product is obtained which appears to be *diphenylpyrazine*, melting at 193° .

On reducing dypnone with sodium amalgam in alcoholic solution, *1-benzoyl-2-phenylpropene*, $\text{CHMePh}\cdot\text{CH}_2\cdot\text{COPh}$, is obtained as crystals melting at 72° and boiling at 200° under 18 mm. pressure; its *phenylhydrazone* melts at $78\text{--}79^\circ$.

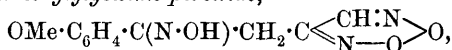
Benzylbenzylidenacetone, $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$, prepared by condensing benzylacetone with benzaldehyde in the presence of sodium hydroxide, crystallises in yellow leaflets melting at 53° ; its *phenylhydrazone* crystallises in yellow needles melting at 116° ; the *oxime* forms small, colourless crystals melting at $95\text{--}105^\circ$. On reduction, benzylbenzylidenacetone is reduced to dibenzylacetone and to a *diketone*, $\text{C}_2\text{H}_2\text{Ph}_2(\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph})_2$, which remains behind on distilling the mixture, and forms crystals melting at $171\text{--}172^\circ$.

Benzylacetylacetone, $\text{CHPh}\cdot\text{CHAc}\cdot\text{COMe}$, prepared by reducing benzylidenacetylacetone by sodium amalgam, is a colourless oil, boiling at $151\text{--}152^\circ$ under 16 mm. pressure, and has a sp. gr. 1.063 at 15° . On reducing methoxybenzylidenacetone, two substances are obtained, *methoxybenzylacetone*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COMe}$, which is an oil boiling at 160° under 22 mm. pressure and has a sp. gr. 1.0504 at 22° ; it forms a *phenylhydrazone* melting at $107\text{--}108^\circ$; the other substance, $\delta\epsilon$ -*dianisylocta- $\beta\gamma$ -dione*, $\text{C}_2\text{H}_3(\text{C}_6\text{H}_4\cdot\text{OMe})_2(\text{CH}_2\cdot\text{COMe})_2$, crystallises in needles melting at $151\text{--}152^\circ$, and yields a *phenylhydrazone*, crystallising in colourless needles melting at 180° .

II. Action of Nitrous and Nitric Acids on $\alpha\beta$ -Unsaturated Aromatic Oximino-compounds.—[With HEINRICH TIETZ].—*Oximinobenzoylmethylglyoxime peroxide*, $\text{OH}\cdot\text{N}:\text{CPh}\cdot\text{CH}_2\cdot\text{C}\begin{smallmatrix} \text{CH}\cdot\text{N} \\ \text{N}\text{---}\text{O} \end{smallmatrix}\text{O}$ (compare Abstr., 1900, i, 504), is prepared by adding an aqueous solution of sodium nitrite to benzylidenacetoxime in acetic acid, and crystallises in red leaflets melting at 215° ; the *sodium* derivative forms lustrous, green crystals, and reduces Fehling's solution; the *acetyl* derivative, prepared by the action of acetic anhydride on the peroxide, crystallises in reddish-yellow needles melting at $150\text{--}154^\circ$. When oxidised with perman-

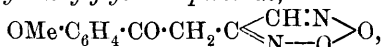
ganate, or heated with hydrochloric or nitric acids, benzoic acid is alone formed. When oxidised by concentrated nitric acid, *p*-nitrobenzoylmethylglyoxime peroxide, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{C} \begin{smallmatrix} \text{CH:N} \\ \text{N-O} \end{smallmatrix} \text{O}$, is formed in small quantity, crystallising in yellow needles melting at $197-198^\circ$; on hydrolysis with hydrochloric acid, *p*-nitrobenzoic acid is alone produced. When benzylideneacetoxime is kept in contact with nitric acid for a long time in the cold, benzoylmethylglyoxime peroxide, $\text{CH}_2\text{Bz} \cdot \text{C} \begin{smallmatrix} \text{CH:N} \\ \text{N-O} \end{smallmatrix} \text{O}$, is produced; it crystallises in reddish-yellow crystals melting at $158-159^\circ$.

p-Methoxybenzylideneacetoxime, which crystallises in needles melting at $119-120^\circ$, is converted by the action of nitrous acid into oximinocanisoylmethylglyoxime peroxide,



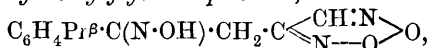
which crystallises in small, red leaflets melting at $197-198^\circ$; its *acetyl* derivative forms brick-red needles melting at $168-169^\circ$.

p-Methoxybenzoylmethylglyoxime peroxide,



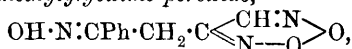
prepared from the corresponding acetoxime and dilute nitric acid, crystallises in brick-red crystals melting at $159-160^\circ$.

Oximinocuminoylmethylglyoxime peroxide,

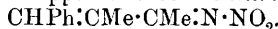


is prepared from cumylideneacetoxime, and crystallises in red needles melting at 187° ; when oxidised with nitric acid, a compound is formed which melts at $87-88^\circ$.

Oximinobenzoyldimethylglyoxime peroxide,



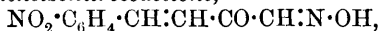
prepared from α -benzylidene-ethylmethylketoxime, crystallises in red leaflets melting at 195° ; its *acetyl* derivative crystallises in orange-yellow needles melting at $146-147^\circ$. γ -Benzylidene-ethylmethylketoxime, when similarly treated, yields a colourless substance, melting at $154-155^\circ$, which appears to be the *nitrimine*,



III. *Action of Oxides of Nitrogen on Oximino-compounds*.—[With W. SLOAN MILLS.] (Compare Abstr., 1902, i, 184, and preceding section).—*Benzylideneisonitrosoacetoxime*, $\text{CHPh} : \text{CH} \cdot \text{C}(\text{N} \cdot \text{OH}) \cdot \text{CH} : \text{N} \cdot \text{OH}$, prepared from benzylideneisonitrosoacetone (obtained from benzaldehyde and isonitrosoacetone) and hydroxylamine, crystallises in long, colourless prisms melting and decomposing at $201-202^\circ$. Attempts to oxidise the acetoxime with nitrous acid were fruitless, but on passing nitrous fumes into the ethereal solution benzylidenemethylglyoxime peroxide nitrosate, $\text{NO}_2 \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{C} \begin{smallmatrix} \text{CH:N} \\ \text{N-O} \end{smallmatrix} \text{O}$, was obtained as white, unstable needles melting at $101-102^\circ$. When heated in benzene, nitrous fumes are evolved, and benzylidenemethylglyoxalketoxime, $\text{CHPh} : \text{CH} \cdot \text{C}(\text{N} \cdot \text{OH}) \cdot \text{CHO}$, is formed; it crystallises in brown needles

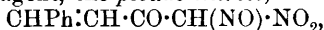
melting at 103—104°, the alkaline solution of which reduces Fehling's solution in the cold; it forms two *semicarbazones*, which can be separated by taking advantage of their different solubility in acetic acid; the soluble *semicarbazone* crystallises in long needles melting and decomposing at 225—226°, and the insoluble *semicarbazone* melts at 242°.

m-Nitrobenzylideneisonitrosoacetone,



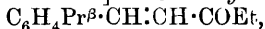
is prepared by treatment of a mixture of *m*-nitrobenzaldehyde and *iso*-nitrosoacetone with warm sodium hydroxide, and forms pale yellow needles melting and decomposing at 164°; the *phenylhydrazone* crystallises in yellow needles melting at 99—100°; when heated with phenylhydrazine (2 mols.), the hydroxylamine is eliminated and a diphenylhydrazone melting at 206—207° is formed. The *oxime* is a white, crystalline powder melting at 220°, and the *semicarbazone* a powder melting and decomposing at 196—197°.

Cuminyldeneisonitrosoacetone, $\text{C}_6\text{H}_4\text{Pr}^\beta\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$, prepared from cuminaldehyde and *isonitrosoacetone*, crystallises in sulphur-yellow plates, melting at 162—163°; its *semicarbazone* is a white powder melting and decomposing at 176°, and the *oxime* crystallises in needles melting and decomposing at 192°. Although nitrous fumes convert benzylideneacetoxime into benzoylmethylglyoxime peroxide, benzylideneisonitrosoacetone yields, when treated in ethereal solution with this reagent, the *pseudo-nitrole*,

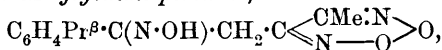


which crystallises in yellow plates melting at 123—124°, reduces Fehling's solution, and gives Liebermann's nitroso-reaction.

IV. *α*- and *γ*-Cuminyldenebutanone and its Transformation Products. —[With THEODOR ST. WARUNIS.]—*α*-Cuminyldenebutanone,

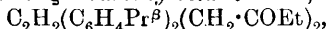


is prepared by shaking cuminaldehyde and methyl ethyl ketone with 33 per cent. sodium hydroxide for ten days and fractionating the oil under reduced pressure, when the ketone boils at 170° under 17 mm. pressure; it crystallises in leaflets melting at 32—33°, has a sp. gr. 0.9875, and n_D 1.56583 at 20°. The *phenylhydrazone* crystallises in needles melting at 87.5°, and the *semicarbazone* in small needles melting at 193° (corr.). The *oxime* could not be isolated in the pure state, but was immediately converted by treatment with sodium nitrite and acetic acid into the *glyoxime peroxide*,



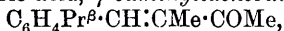
which forms large crystals melting and decomposing at 166°. *Dibromo-α-cuminyldenebutanone*, $\text{C}_{14}\text{H}_{18}\text{OBr}_2$, prepared from the ketone and bromine in acetic acid solution, crystallises in colourless needles melting at 141° (corr.).

On reduction, *α*-cuminyldenebutanone is converted into *α*-cuminyldenebutanone, $\text{C}_6\text{H}_4\text{Pr}^\beta\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COEt}$, which is an oil boiling at 160—164° under 17 mm. pressure, and has a sp. gr. 0.9582 and n_D 1.51321 at 20°, and $\epsilon\zeta$ *dicumenylocta-εθ-dione*,

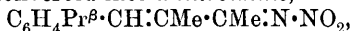


which remains after the distillation of the butanone, and crystallises in white needles melting at 169.5° (corr.).

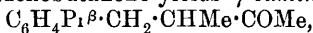
When cuminaldehyde and methyl ethyl ketone are condensed in the presence of hydrochloric acid, γ -cuminyldenebutanone,



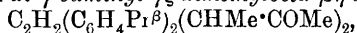
is obtained as an oil boiling at 171.5° (corr.) under 17 mm. pressure and having a sp. gr. 0.9858 and n_D 1.56512 at 22° ; the semicarbazone crystallises in rhombic leaflets melting at 177.5° (corr.), and the phenylhydrazone in white needles melting at 106.5° (corr.), and the oxime in large, monoclinic prisms melting at 116.5° (corr.). Under the influence of nitrous acid, the oxime is converted into a nitroimine,



crystallising in rhombic plates, melting and decomposing at 169.5° (corr.). Dibromo- γ -cuminyldenebutanone was only obtained as an oil. On reduction, γ -cuminyldenebutanone yields γ -cuminyldbutanone,



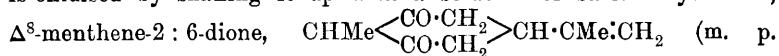
which is obtained as an oil boiling at 155.5° (corr.) under 16 mm. pressure, and having a sp. gr. 0.9560 and n_D 1.51284 at 20° ; its semicarbazone crystallises in leaflets melting at 148.5° (corr.); the other product of the reduction, $\delta\epsilon$ -di- γ -cuminyl- $\gamma\zeta$ -dimethylocta- $\beta\eta$ -dione,



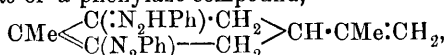
crystallises in rhombic plates melting at 145.5° (corr.).

Since hypochlorous acid oxidises ketones of the type $\text{R}\cdot\text{CH}\cdot\text{CMe}\cdot\text{COMe}$ to acids with one carbon atom less, whilst ketones of the type $\text{R}\cdot\text{CH}\cdot\text{CH}\cdot\text{COEt}$ are not attacked (compare Stoermer and Wehler, 1903, i, 40), it is possible to distinguish between the α - and γ -cuminyldene compounds; the α -compound is unchanged, but the γ -compound is oxidised to α -methyl- p -isopropylcinnamic acid (Perkin, Trans., 1877, 31, 791).

V. Auto-oxidation Products of Carvone.—[With ARTHUR STÄHLER.] (Compare Abstr., 1898, i, 568; and 1901, i, 551).—When d -carvone is oxidised by shaking it up with a solution of barium hydroxide,



187–1883, *loc. cit.*), is formed in small quantity; the same diketone is also obtained by oxidising l -carvone in a similar manner. The menthenedione is inactive, a fact which is worthy of notice, since, if it were a keto-enolic compound, it would be expected to be optically active. d -Carvonehydroxylamino-oxime (compare Harries and Mayrhofer, Abstr., 1899, i, 624), the melting point of which is now found to be 106° , was converted into the dioxime (m. p. 192° . Compare *loc. cit.*), which, on hydrolysis with dilute sulphuric acid, yields Δ^8 -menthene-2:6-dione. This diketone, which does not combine with phenylcarbimide as does the nearly related methylidihydroresorcinol, is readily converted into the dioxime from which it was formed, and into a semicarbazone which forms crystals melting at 235° . Phenylhydrazine reacts with the menthenedione in a complicated manner, giving the phenylhydrazone of a phenylazo-compound,

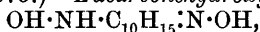


which crystallises in garnet-red needles melting at 147° . 8-Bromo

mentha-2:6-dione, prepared by dissolving the menthenedione in a solution of hydrogen bromide in acetic acid, crystallises in leaflets melting at 135°. When boiled with a methyl-alcoholic solution of potassium hydroxide, hydrogen bromide is eliminated, Δ^4 -*menthene-2:6-dione* being produced, crystallising in long needles melting at 157°. It forms an additive product with hydrogen bromide, which is identical with the 8-bromo-compound.

Δ^8 -Menthenedione is also obtained from *l*-carvoneoxamino-oxime; the latter is obtained as crystals melting at 109° by Harries and Mayrhofer's method; its *hydrochloride* is a hygroscopic crystalline powder; its *dibenzoyl* derivative forms prisms melting at 168°, and its *diphenylcarbamide* crystallises in needles melting at 152°. The diphenylcarbamide from *d*-carvoneoxamino-oxime was erroneously described as melting at 97° instead of 161°. On oxidation by the air, the hydroxylamino-oxime is converted into the dioxime (m. p. 188°), which yields a *dibenzoyl* derivative melting at 129° (compare Harries and Mayrhofer, who record the melting point as 118—120°). The dioxime is converted on hydrolysis into the menthenedione.

Eucarvone.—[With ARTHUR STÄHLER.] (Compare Baeyer, Abstr., 1894, i, 435; 1898, i, 675.)—*Eucarvonehydroxylamino-oxime*,



is prepared by keeping eucarvone and hydroxylamine in methyl-alcoholic solution for eight days, and then, after removal of the solvent, converting the hydroxylamino-oxime into an *oxalate*; an acid and a neutral oxalate are formed, the latter being readily isolated, as it is insoluble in water, melting at 198°; *hydroxylamino-oxime* forms crystals melting at 141—142°. The *picrate* crystallises in yellow needles, and the *diphenylcarbamide* forms crystals melting at 157°. No evidence was obtained for the view that the eucarvone contains a trimethylene ring.

K. J. P. O.

Stereoisomeric Oximes of Dypnone. FERD. HENRICH and A. WIRTH (*Ber.*, 1904, 37, 731—734. Compare Delacre, *Bull. Acad. Belg.*, 1890, [iii], 20, 471, and Harries and Gollnitz, preceding

abstract).—*syn-Dypnoneoxime*, $\text{CMePh}\cdot\text{CH}\cdot\overset{\text{CPh}}{\underset{\text{N}\cdot\text{OH}}{\parallel}}$, prepared by boiling

an alcoholic solution of dypnone with hydroxylamine hydrochloride (1 mol.) for 5 hours, crystallises from alcohol in thick plates, melts at 134°, and undergoes the Beckmann transformation, forming β -*methylcinnamoylanilide*, $\text{CMePh}\cdot\text{CH}\cdot\text{CO}\cdot\text{NHPh}$, which crystallises from dilute alcohol or light petroleum in white leaflets and melts at 121°. When the *syn*-oxime is heated for an hour on the water-bath with concentrated sulphuric acid, it is converted into *anti-dypnoneoxime*, $\text{CMePh}\cdot\text{CH}\cdot\overset{\text{CPh}}{\underset{\text{N}}{\parallel}}$,



which is also obtained by heating dypnone with an alcoholic solution of hydroxylamine hydrochloride containing potassium hydroxide; it crystallises from ether in slender, white needles, melts at 78°, and does not undergo the Beckmann transformation.

W. A. D.

Aromatic Ketones. HEINRICH WIELAND (*Ber.*, 1904, 37, 1142—1148. Compare Dimroth, *Abstr.*, 1903, i, 629).—An attempt was made to prepare aromatic hydrocarbons of the allylene series from ketones derived from diphenylpropane by conversion into ketochlorides and removal of hydrogen chloride.

Dibenzyl ketone, prepared by distilling calcium phenylacetate under reduced pressure, reacts with phosphorus pentachloride, forming *β*-chloro-*α*-diphenylpropylene, $\text{CH}_2\text{Ph}\cdot\text{CCl}\cdot\text{CHPh}$, a yellow oil, boiling at 181° under 12 mm. pressure, together with small quantities of crystalline products. Potassium hydroxide in methyl alcohol converts the chloro-compound into a hydrocarbon, $\text{C}_{15}\text{H}_{12}$, which crystallises from alcohol as a bulky, white powder, becoming yellow in the air, and melts at 121.5° . It may be diphenylallylene, $\text{CHPh}\cdot\text{C}\cdot\text{CHPh}$, or phenylbenzylacetylene, $\text{CPh}\cdot\text{C}\cdot\text{CH}_2\text{Ph}$, but the quantity obtained was too small for a study of its reactions.

Düisonitrosodibenzyl ketone, $\text{CO}(\text{CPh}\cdot\text{N}\cdot\text{OH})_2$, prepared by the action of sodium and amyl nitrite on dibenzyl ketone, crystallises from chloroform in bright green leaflets and melts at 133.5° .

Dibenzyl ketone and cinnamaldehyde condense in presence of a small quantity of diethylamine to 2 : 5 : 6-triphenylcyclo- Δ^2 -hexene-1-one, $\text{CPh}\cdot\text{CO}\cdot\text{CHPh}$
 $\text{CH}\cdot\text{CH}_2\cdot\text{CHPh}$, which separates from alcohol in colourless crystals, melts and decomposes at $181\text{—}191^\circ$, and dissolves sparingly in alcohol, ether, or light petroleum, readily in benzene or chloroform; it decolorises potassium permanganate and yields a waxy additive product with bromine. Tin and hydrochloric acid do not reduce it, but convert it into an *isomeride*, crystallising from alcohol in colourless needles and melting at 136° ; it is more soluble than the former compound.

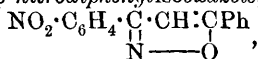
Benzylideneacetophenone polymerises under the influence of acetic anhydride and sulphuric acid, forming a dimolecular compound, which crystallises from alcohol in glistening, white needles and melts at 134° . It does not take up bromine, and is probably a tetramethylene derivative, $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{Ph}$
 $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{Ph}$ C. H. D.

p-Nitrodibenzoylmethane. HEINRICH WIELAND (*Ber.*, 1904, 37, 1148—1152).—The course of the reaction by which dibromides containing the group $-\text{CHBr}\cdot\text{CHBr}-$ are converted into the corresponding ketones $-\text{CO}\cdot\text{CH}_2-$ has been explained by Thiele and Haeckel (*Abstr.*, 1903, i, 160). In the present paper, an intermediate product has also been isolated confirming this view.

p-Nitrobenzylideneacetophenone dibromide,
 $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{COPh}$,
 crystallises in nacreous leaflets and melts at 151° (compare Sorge, *Abstr.*, 1902, i, 379). Ammonia converts it into yellow crystals of
 $\text{COPh}\cdot\text{CH}\cdot\text{NH}\cdot\text{CH}\cdot\text{COPh}$
 the corresponding *piperazine*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{NH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$,
 melting at 141° and yielding a crystalline nitrosoamine with nitrous acid.

Potassium hydroxide in methyl-alcoholic solution converts the

dibromide into an *acetal*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{OMe})_2 \cdot \text{CH}_2 \cdot \text{COPh}$, which crystallises from alcohol in large, colourless tablets and melts at 91° . Acids in the cold, and alkalis on warming, convert it into *p-nitrodibenzoylmethane*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{COPh}$, crystallising from alcohol in yellow needles and melting at 160° , dissolving readily in benzene, more sparingly in alcohol or chloroform. The alkali salts are precipitated from alcohol in orange scales. Ferric chloride produces a red coloration, copper acetate precipitates a yellow copper salt. Hydroxylamine forms *p-nitrodiphenylisooxazole*,



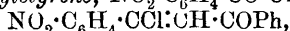
which crystallises from glacial acetic acid in glistening, yellow leaflets, sparingly soluble in all solvents, and melts at 221° .

Hydrazine yields *p-nitrodiphenylpyrazole*,

$$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \underset{\text{N} \text{---} \text{NH}}{\overset{\text{||}}{\text{C}}} \cdot \text{CH} \cdot \text{CPh},$$

which forms silky, yellow needles and melts above 250° . Reduction yields the *amino*-base melting at 179° ; the *hydrochloride* chars at 235° .

Phosphorus pentachloride converts *p-nitrodibenzoylmethane* into *α-chloro-ω-p-nitrobenzoylstyrene*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH} \cdot \text{CClPh}$ or



which crystallises from methyl alcohol in yellow tablets and melts at 131° .
C. H. D.

Condensation Products from Anthraquinone-β-sulphonic Acid and Primary Aromatic Amines. FÄRBFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 147277).—Condensation products are obtained on heating anthraquinone-β-sulphonic acid with primary aromatic amines, preferably in presence of a condensing agent, such as boric acid, and of a reducing agent, such as stannous chloride. The *compound* from anthraquinone-2-sulphonic acid and aniline crystallises from pyridine in orange needles and dissolves in hot alcohol or acetic acid. The solution in concentrated sulphuric acid is yellow, and has an intense blue fluorescence, which disappears on heating. Similar products are obtained from *o*-toluidine and *m*-xylidine.
C. H. D.

Nitro-nitroamines and Nitroamines of the Anthraquinone Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 146848 and 148109).—The action of nitric acid in limited quantity on diamino- or dialphylidiamino-anthraquinones and their sulphonic acids leads to substitution in the anthraquinone ring, an excess of nitric acid reacts with the amino- or imino-groups present, forming nitroamines, containing the group $-\text{NH} \cdot \text{NO}_2$ or $-\text{N}(\text{aliphyl}) \cdot \text{NO}_2$. These nitroamines are unstable and explosive, and the nitro-group is partially or entirely eliminated from them on boiling with nitrobenzene, aromatic hydrocarbons, or other indifferent solvents, or by the action of phenols or aminoanthraquinones in concentrated sulphuric acid at the ordinary temperature.

1:5-Diaminoanthraquinone yields dinitrodiamino-, tetranitrodiamino-, or tetranitrodinitroamino-anthraquinone on nitration, ac-

according to the quantity of nitric acid employed. Tetrabromo-1:5-diaminoanthraquinone yields only tetrabromodinitroaminoanthraquinone, no nitration taking place in the ring. When a mixture of sulphuric and nitric acids is employed, sulphonation also occurs. The patent contains the colour-reactions of a large number of nitration products.

Dibromodinitro-1:5-diaminoanthraquinone, prepared by heating dibromodinitro-1:5-dinitroaminoanthraquinone with phenol or cuminol, crystallises from phenol or nitrobenzene in green, metallic needles, melts above 300°, and forms red solutions. Sodium sulphide reduces it to an indigo-blue *dibromotetraminoanthraquinone*. *Nitro-β-aminoanthraquinone* is a yellow, insoluble powder.

Tetranitro-1:5-diaminoanthraquinone, prepared from tetranitro-1:5-dinitroaminoanthraquinone and 1:5-diaminoanthraquinone in cold concentrated sulphuric acid solution, is a dark violet powder, which decomposes on heating. *Tetrabromo-1:5-diaminoanthraquinone*, which may be prepared by saturating an alcoholic solution of tetrabromo-1:5-dinitroaminoanthraquinone with hydrogen chloride and heating, separates in red crystals.

C. H. D.

1-Nitro-5- and -8-aminoanthraquinones. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 147851).—Dinitroanthraquinones have not hitherto been partially reduced to nitroaminoanthraquinones, but this reduction may be effected by heating with aromatic mono- or di-alkylamines. Thus, on boiling 1:5-dinitroanthraquinone with dimethylaniline or similar base, a blood-red solution is obtained, from which 1-nitro-5-aminoanthraquinone separates in garnet-red prisms on cooling. It dissolves in fuming sulphuric acid to a reddish-violet solution, 1-nitro-8-aminoanthraquinone forms a yellow solution. The constitution of these compounds is confirmed by reduction to diaminoanthraquinones, and by conversion into dihydroxyanthraquinones.

C. H. D.

[**Arylaminoanthraquinones.**] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 148767. Compare Abstr., 1902, i, 476).—The acyl derivatives of 4-nitro-1-aminoanthraquinones condense with aromatic amines more readily than the free bases, and the acyl group may then be readily removed by means of acids.

1-Acetyl-amino-4-p-toluidinoanthraquinone, from 1-acetyl-amino-4-nitroanthraquinone and p-toluidine, crystallises from pyridine in broad, dark-violet needles with greasy lustre and melts at 193°. It is insoluble in water, but dissolves in organic solvents. The compound from 1:5-diacetyl-amino-4:8-dinitroanthraquinone and aniline is bluish-violet and melts and decomposes above 300°. The solution in concentrated sulphuric acid is colourless, and hydrolysis occurs gradually.

C. H. D.

Preparation of Leucohydroxyanthraquinones. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 148792).—The reduction of 4-nitro-1-hydroxyanthraquinone derivatives or of 4-nitro-1-aminoanthraquinones in acid solution with an excess of reducing agent pro-

duces leuco-compounds in which the amino-group is very readily replaced by hydroxyl on heating. In the case of ethers, the ether group is removed. Sulpho-groups or halogen atoms, if present in the same ring as the nitro-radicle and the hydroxy- or amino-group, are also replaced by hydrogen. The leucohydroxyanthraquinones are yellow or brown, and dissolve in alkalis to yellow solutions, oxidising in contact with air. The appearance and colour-reactions of a number of leuco-compounds are described. C. H. D.

Preparation of Amino-5- and -8-hydroxyanthraquinones. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 148875).—1-Aminoanthraquinone-5- and -8-sulphonic acids, prepared by successive nitration and reduction of anthraquinone-*a*-sulphonic acid, may be separated by means of dilute acetic acid, in which the 1:5-compound is the more soluble. Heating with hydroxides of the alkali earths under pressure converts them into 1-amino-5-hydroxyanthraquinone, crystallising from benzene in red, metallic prisms, melting at 210°, and dissolving sparingly in water, but more readily in alcohol or acetone, and 1-amino-8-hydroxyanthraquinone, crystallising from benzene in long, brown needles and melting at 230°. The 1:5-compound forms an *acetyl* derivative, crystallising in needles, and a *diacetyl* derivative, forming yellow, glistening leaflets. Fusion with oxalic acid forms an *oxamic acid* crystallising in yellow prisms. C. H. D.

Metal-organic Syntheses of the Acyl Camphors. JULIUS W. BRÜHL (*Ber.*, 1904, 37, 746—761).—Claisen's method of preparing formylcamphor (hydroxymethylenecamphor) by the action of sodium on a mixture of camphor and an alkyl formate gives only traces of acetylcamphor when the alkyl formate is replaced by an alkyl acetate. Forster's method for preparing benzoylcamphor also cannot be used for the preparation of acetylcamphor, as this compound is only produced in small quantities when acetic anhydride, chloride, or bromide is allowed to act on sodium camphor; the main products of the action when acetyl chloride is allowed to act on sodium camphor are bornyl acetate and the acetate of enolic camphor; these were not separated, but their presence was indicated by the formation of both borneol and camphor by alkaline hydrolysis.

In confirmation of Malmgren's observations, it has been found (1) that magnesium acts on bromocamphor in ethereal solution, giving two magnesium-organic compounds, one soluble and the other insoluble in ether; (2) that a similar action takes place in boiling xylene solution; no hydrogen is liberated, although a certain amount of hydrogen bromide is eliminated from the bromocamphor, and the products are camphor, borneol, and Oddo's dicamphoquinone, $(C_{10}H_{14}O)_2$; (3) that the magnesium compound gives camphocarboxylic acid when acted on by carbon dioxide, acetylcamphor, and (?) acetylcamphenol acetate,

$C_8H_{14} \begin{smallmatrix} \text{CAc} \\ | \\ \text{COAc} \end{smallmatrix}$. The insoluble magnesium-organic compound is probably not a mixture of magnesium camphor and magnesium bromide, $(C_{10}H_{15}O)_2Mg, MgBr_2$, as Malmgren supposed, for magnesium bromide forms soluble ether compounds, but may be regarded as the enolic

magnesium compound, $C_8H_{14} \begin{smallmatrix} CH \\ | \\ C \cdot OMgBr \end{smallmatrix}$. Whilst the magnesium-organic compounds of iodo- and bromo-camphocarboxylic esters yield carbon-ethers with acetyl haloids and only oxygen-ethers with acyl esters, the magnesium compound from bromocamphor gives acylcamphors by the action of acyl haloids, and an even simpler method of preparing acetylcamphor consists in allowing magnesium (1 atom) to act on a solution of bromocamphor (1 mol.) in an excess of ethyl acetate; the acetylcamphor is extracted by means of soda, and the tertiary carbinol and camphor remain in the insoluble layer; the yield of acetylcamphor, when using acetyl chloride or bromide, is at the most 8 per cent., but, when using methyl or ethyl acetate, may be as much as 20 or 21 per cent. of the theoretical quantity (Malmgren obtained 37 per cent.).

Camphocarboxylic acid could not be obtained by the action of zinc on bromocamphor in presence of carbon dioxide, but a very favourable yield of acetylcamphor was obtained by using zinc.

The best results are obtained in ethereal solution; the yield, with granulated zinc, bromocamphor, and ethyl acetate, was 16—17 per cent. in ethereal solution, and 9—10 per cent. in xylene solution; by using zinc dust in place of granulated zinc, the yield in ethereal solution was raised to 35 per cent.; a yield of 14—15 per cent. was obtained from iodocamphor and ethyl acetate in xylene.

aa'-Dibromocamphor gave, with magnesium and ethyl acetate, *α*-bromocamphor, acetylcamphor, and acetylcamphenol acetate, but no *aa'*-diacetylcamphor.

Bromoformylcamphor is also reduced in a similar manner to hydroxymethylenecamphor. T. M. L.

Chemical and Physical Properties and Constitution of the Acylcamphors. JULIUS W. BRUHL (*Ber.*, 1904, 37, 761—773).—The boiling points of the series are:

| | B. p. | Pressure. |
|---------------------------------|-----------|-----------|
| Hydroxymethylenecamphor ... | 105° | 11·0 mm. |
| Acetylcamphor | 118—118·5 | 11·2 „ |
| „ | 127—128 | 15·5 „ |
| Propionylcamphor* | 129 | 11·0 „ |
| Butyrylcamphor * | 132—133 | 11·2 „ |
| „ | 134—135 | 12·0 „ |
| <i>iso</i> Valerylcamphor | 141—148 | 11·0 „ |

Only the first member of the series is solid. It has a camphor-like smell, whilst the odour of acetylcamphor resembles rather that of menthol; the higher homologues have a feeble and less characteristic odour, but still suggestive of menthol.

Hydroxymethylenecamphor liberates acetic acid from its salts, dissolves in the calculated quantity of sodium hydroxide solution, and also dissolves in sodium carbonate and even in sodium hydrogen

* Malmgren's boiling points are about 10° higher.

carbonate; acetylcamphor is much less acid; acetylcamphor also dissolves in the calculated quantity of aqueous sodium hydroxide, but the solution is strongly alkaline and becomes cloudy as it absorbs carbon dioxide from the air. When titrated with sodium hydroxide and phenolphthalein, the colour appeared when 18 per cent. of the theoretical amount of normal, and 20 per cent. of decinormal, sodium hydroxide still remained to be added; with litmus and decinormal sodium hydroxide, the end-point was reached when only 21 per cent. of the theoretical amount of alkali had been added. Acetylcamphor is soluble in sodium carbonate solution, but requires 13 times the theoretical quantity of alkali. It can, however, still be readily extracted from ether by means of alkalis. Propionylcamphor also dissolves in the calculated quantity of sodium hydroxide solution, but gives a coloration with phenolphthalein and sodium hydroxide when only 54 per cent. of the theoretical quantity of alkali is added; it no longer acts on blue litmus, but can be extracted from ethereal solution by twice normal sodium hydroxide. Butyrylcamphor is still less acid in its properties, and can only be extracted with difficulty from its ethereal solution by twice normal sodium hydroxide, whilst valerylcamphor requires 50 per cent. potassium hydroxide for this purpose, and can then be only extracted partially.

Hydroxymethylenecamphor forms an acid and a normal copper salt, acetylcamphor only a *normal copper* salt, which crystallises from light petroleum in glistening, dark olive-green flakes and melts at 201—202°. The higher homologues also form only the normal copper salts.

The sp. gr., mol. vol., refractive index for the three hydrogen lines and the D line, molecular refraction, and dispersion are tabulated in the original paper for acetylcamphor, propionylcamphor, butyrylcamphor, and isovalerylcamphor.

The conclusion is drawn that all the members of the series exist exclusively, like hydroxymethylene camphor, in the keto-enolic form, as hydroxyalkylidene compounds, $C_8H_{14} \begin{smallmatrix} \diagup C:CR \cdot OH. \\ \diagdown CO \end{smallmatrix}$ T. M. L.

Anhydrohydroxylamine Unsaturated Ketones. FRIEDERICH W. SEMMLER (*Ber.*, 1904, 37, 950—957).—On heating pulegone-hydroxylamine with concentrated acids at from 50—100°, amongst other products, a weak base, *α-anhydropulegonehydroxylamine*, $C_{10}H_{17}ON$, is formed. This boils at 91° under 8 mm. pressure, has a sp. gr. 0.9731 at 20°, n_D in a 10 mm. tube + 37°10', $n_D = 1.4757$, so that the molecular refraction is 48.38 indicating the presence of a dicyclic system in the compound. It shows most of the reactions of the alkaloids. The *oxime*, $C_{10}H_{17}N:N$, melts at 181°, and is soluble both in acids and alkalis; the *semicarbazone*, $C_{10}H_{17}N:N \cdot NH \cdot CO \cdot NH_2$, melts at 153—154°; the *benzenesulphonyl base*, $C_6H_5SO_2 \cdot C_{10}H_{16}NO$, which melts at 120°, and is insoluble even in concentrated alkali; the *methyl base*, $C_{10}H_{16}MeON$, boils at 102—104° under 9 mm. pressure, has a sp. gr. 0.968 at 20°, and n_D 1.480, and forms a *picrate* melting at 170°. These reactions point to the compound being a saturated ketoimine base.

On reduction with sodium and alcohol, a *tetrahydro-base*, $C_{10}H_{21}ON$, is formed which boils at $134-135^{\circ}$ under 18 mm. pressure, has a sp. gr. 0.9646 at 20° , and $n_D = 1.4815$. It does not form a sparingly soluble picrate. When zinc dust and hydriodic acid were used for the reaction, a *base*, $C_{10}H_{19}ON$, was formed, boiling at 106° under 11 mm. pressure and having a sp. gr. 0.952 at 20° ; this gave a thiocarbamide melting at 201° . The *base*, $C_{10}H_{17}ON$, forms a *thiocarbamide*, $NHPh \cdot CS \cdot N \cdot C_{10}H_{16}O$, melting at 134° , and a *picrate* melting at 152° .
E. F. A.

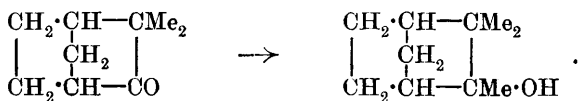
Thujyl Derivatives. IWAN L. KONDAKOFF and V. SKWORZOFF (*J. pr. Chem.*, 1904, 69, 176—186. Compare Abstr., 1902, i, 807; 1903, i, 642).—Thujene, when treated with halogen acids, gives a certain quantity of liquid dihalogen compounds; this is probably formed from *isothujene* present; the yield is small when the thujene has been prepared by the xanthate method, but considerable in the case of thujene prepared from thujyl haloids. In the latter case, the dibromide, as well as the dichloride, was treated with aqueous alcohol; after half a year, no formation of a terpin had occurred (von Baeyer, Abstr., 1894, i, 92). The main product, $C_{10}H_{18}Br_2$, boiled at $134-135^{\circ}$ under 11 mm. pressure, and lost 2HBr when heated with alcoholic potassium hydroxide at 120° , yielding a hydrocarbon that boiled at $179-185^{\circ}$ and had a sp. gr. 0.8449 at $18^{\circ}/4^{\circ}$, n_D 1.48074, and $[\alpha]_D - 0.38'$.

The author defends his formula for thujone (Abstr., 1902, i, 807) against the criticisms of Tschugaeff (*Chem. Zeit.*, 1903, 27, 970) and Semmler (*Ber.*, 1903, 36, 4367).
C. F. B.

Camphene. GEORG WAGNER, ST. MOYCHO, and FR. ZIENKOWSKI (*Ber.*, 1904, 37, 1032—1037).—Large quantities of camphene were oxidised by 4 per cent. aqueous potassium permanganate at 60° , the neutral products isolated being camphenylone, campheneglycol, and a *compound*, $C_{10}H_{16}O_2$; the acid products are camphenecamphoric acid and camphenylic acid. The *compound*, $C_{10}H_{16}O_2$, crystallises from ether in beautiful plates, melts at $169-170^{\circ}$, and is indifferent to hydroxylamine, semicarbazide, and Fehling's solution; on further oxidation with potassium permanganate, it gives a *ketone* which is volatile with steam, and yields a *semicarbazone* melting at 184.5° , together with two *acids* having the composition $C_{10}H_{14}O_3$ and $C_{10}H_{16}O_4$, melting respectively at $197-198^{\circ}$ and 203° . The oxidation products of the compound $C_{10}H_{16}O_2$ are thus quite different from those of campheneglycol. Campheneglycol when pure melts at $199-200^{\circ}$.

Small quantities of the unchanged hydrocarbon cyclene, $C_{10}H_{16}$ (Wagner and Godlewski, *J. Russ. phys. Chem. Soc.*, 1897, 29, 121), remain after the whole of the camphene has been oxidised; it is probable, therefore, that the dehydrating action of zinc chloride on *isoborneol* gives rise, in addition to camphene, to a small quantity of cyclene.

Assuming Wagner's formulæ, camphenylone should give *isoborneol* when treated with methyl iodide and magnesium, thus:



Actually, however, a new *alcohol*, $\text{C}_{10}\text{H}_{17}\cdot\text{OH}$, is formed, which crystallises from light petroleum, melts at $117.5-118^\circ$, boils and partially decomposes at $204-206^\circ$, and with phenylcarbimide gives a *urethane* which melts at $127.5-128^\circ$. With glacial acetic acid and sulphuric acid, it gives a mixture of camphene and, probably, *isobornyl acetate*. It is apparently optically inactive. W. A. D.

New Constituents of Oil of Roses. HUGO VON SODEN and WALTER TREFF (*Ber.*, 1904, 37, 1094—1095. Compare *Abstr.*, 1901, i, 39, 733).—Some 5—10 per cent. of nerol (*Abstr.*, 1903, i, 267) has been obtained from oil of roses; it is slightly optically active owing to the presence of small amounts of citronellal (?). About 1 per cent. of eugenol and a *sesquiterpene alcohol*, $\text{C}_{15}\text{H}_{26}\text{O}$, have also been isolated; the latter distils at 149° under 4 mm. pressure, has a sp. gr. 0.894 at 15° , is optically inactive, and closely resembles farnesol. J. J. S.

Blue Dyes of the Anthracene Series. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 145237).—The disulphonic acids of dinitro-anthrachryson dialkyl ethers (*Abstr.*, 1903, i, 840) may be reduced by stannous chloride or sodium sulphide to diaminoanthrachryson dialkyl ether disulphonic acids, which form dark blue, crystalline alkali salts, dissolving in water to pure blue solutions, becoming greenish-blue on addition of alkali hydroxides. The salts dissolve in concentrated sulphuric acid to orange-coloured solutions, becoming blue on dilution with water. C. H. D.

Brown Colouring Matter of Algæ (Phycophain and Phycoxanthin). N. GAIDUKOV (*Chem. Centr.*, 1904, i, 667; from *Ber. Deutsch. bot. Ges.*, 21, 535—539).—The position of the absorption band of phycophain, the brown colouring matter of the *Phaeophyceæ*, observed by Hansen (*Arb. Bot. Inst. Würzburg*, 3, No. 11) between the lines *b* and *F*, has been quantitatively determined. The fact that the brown colour of the alcoholic extract of the brown and bluish-green algæ is not due to the presence of another dye, phycoxanthin, but depends entirely on the solubility of phycophain, has also been confirmed. Phycophain is not only soluble in boiling, but also in cold, water, and in dilute alcohol, hence, whilst a 97 per cent. solution of alcohol extracts the dye from the wet algæ, it fails to do so from the dry. Phycoxanthin is a mixture of phycophain and carotin, or of chlorophyll and carotin. The author terms phycophain “brown phycochrome,” and by a change of definition “phycochrome Nageli” is relegated to the phycochrome groups to which the chromatophores of the dead algæ and chlorophyll and carotin also belong. The dyes isolated from the algæ are not always identical with those of the chromatophores, thus the green fluorescence of the aqueous extract of *Dictyota dichotoma*, which in the living state is fluorescent and has an absorption band at $\lambda 545$, soon disappears after

filtration, and the brown dye contained in the extract shows the absorption bands of phycophain. Phycophain is also contained in the rhodophycæ. E. W. W.

Synthesis of 2-Hydroxyflavonol. STANISLAUS VON KOSTANECKI and VICTOR LAMPE (*Ber.*, 1904, 37, 773—778).—*Quinacetophenone monomethyl ether*, $\text{OMe} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{COMe}$, prepared by the action of sodium hydroxide on a mixture of quinacetophenone and methyl sulphate, crystallises from dilute alcohol in pale yellow crystals and melts at 52° . When treated with sodium hydroxide and benzaldehyde, it

yields 6-methoxyflavanone, $\text{OMe} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} - \text{CHPh} \\ \diagdown \quad | \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix}$, which crystallises from alcohol in white needles and melts at $141-142^\circ$; its solution in dilute alcohol shows a blue fluorescence. 3-iso*Nitroso-6-methoxyflavanone*, $\text{OMe} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} - \text{CHPh} \\ \diagdown \quad | \\ \text{CO} \cdot \text{C} : \text{NOH} \end{smallmatrix}$, prepared by the action of amyl nitrite on the preceding compound, crystallises from benzene in yellow needles and melts and decomposes at 160° .

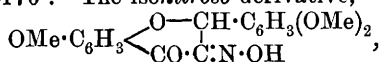
6-Methoxyflavonol, $\text{OMe} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} - \text{CPh} \\ \diagdown \quad | \\ \text{CO} \cdot \text{C} \cdot \text{OH} \end{smallmatrix}$, prepared by hydrolysing the preceding oxime, crystallises from alcohol in pale yellow needles and melts at $204-205^\circ$; it forms a sparingly soluble, yellow sodium salt like the 1-hydroxyflavones, and colours mordanted cotton exactly in the same manner as kaempferide and kaempferol (*Abstr.*, 1889, 868); when boiled down with 50 per cent. potassium hydroxide, it is decomposed, yielding quinol and benzoic acid. The *acetyl* derivative, $\text{OMe} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} - \text{CPh} \\ \diagdown \quad | \\ \text{CO} \cdot \text{C} \cdot \text{OAc} \end{smallmatrix}$, crystallises from alcohol in stout, pure white needles, and melts at $164-166^\circ$.

6-Ethoxyflavonol, $\text{OEt} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} - \text{CPh} \\ \diagdown \quad | \\ \text{CO} \cdot \text{C} \cdot \text{OH} \end{smallmatrix}$, crystallises from alcohol in yellow spangles and melts at $177-178^\circ$. Its *acetyl* derivative, $\text{C}_{19}\text{H}_{16}\text{O}_5$, crystallises from dilute alcohol in colourless needles and melts at $133-134^\circ$.

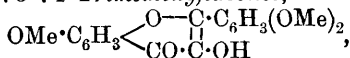
6-Hydroxyflavonol, $\text{OH} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} - \text{CPh} \\ \diagdown \quad | \\ \text{CO} \cdot \text{C} \cdot \text{OH} \end{smallmatrix}$, prepared by the action of hydriodic acid on the methyl ether, crystallises from 50 per cent. alcohol in colourless needles, melts at $233-234^\circ$, and yields a greenish-yellow solution in alkali hydroxides. The *diacetyl* derivative, $\text{C}_{19}\text{H}_{14}\text{O}_6$, crystallises from alcohol in colourless needles and melts at $195-196^\circ$. The *dimethyl ether*, $\text{C}_{17}\text{H}_{14}\text{O}_4$, crystallises from alcohol in colourless, silky needles, and melts at $128-129^\circ$. T. M. L.

Synthesis of an Isomeride of Fisetin. STANISLAUS VON KOSTANECKI and S. KUGLER (*Ber.*, 1903, 37, 779—781).—6 : 3' : 4'-*Trimethoxyflavanone*, $\text{OMe} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} - \text{CH} \cdot \text{C}_6\text{H}_3(\text{OMe})_2 \\ \diagdown \quad | \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix}$, prepared by the action of sodium hydroxide on quinacetophenone monomethyl ether

veratraldehyde, crystallises from alcohol in colourless spangles and melts at 175—176°. The *isonitroso*-derivative,



crystallises from benzene in yellow needles and melts and decomposes at 168°. 6:3':4'-*Trimethoxyflavonol*,

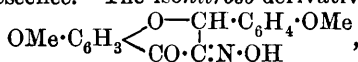


prepared by hydrolysing the preceding oxime, crystallises from alcohol in minute, pale-yellow needles and melts at 189—190°. The *acetyl* derivative, $\text{C}_{20}\text{H}_{18}\text{O}_7$, crystallises from dilute alcohol in rosettes of small, colourless needles and melts at 140—141°. 6:3':4'-*Trihydroxyflavonol*, $\text{OH} \cdot \text{C}_6\text{H}_3 \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \cdot \text{C}_6\text{H}_3(\text{OH})_2 \\ | \\ \text{CO} \cdot \text{C} \cdot \text{OH} \end{array}$, isomeric with fisetin,

prepared by the action of hydriodic acid on the trimethyl ether, crystallises from alcohol in minute, yellow needles, melts and decomposes at 335°, and dyes cotton orange-yellow with aluminium, and olive-brown with iron mordants. The *tetra-acetyl* derivative, $\text{C}_{23}\text{H}_{18}\text{O}_{10}$, forms colourless needles, melts at 197—198°, and is sparingly soluble in alcohol.

T. M. L.

Synthesis of 2:4'-Dihydroxyflavonol. STANISLAUS VON KOSTANECKI and M. L. STOPPANI (*Ber.*, 1904, 37, 781—784).—6:4'-*Dimethoxyflavanone*, $\text{OMe} \cdot \text{C}_6\text{H}_3 \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe} \\ | \\ \text{CO} \cdot \text{CH}_2 \end{array}$, prepared from quinacetophenone monomethyl ether and anisaldehyde, crystallises from alcohol in long, colourless needles and melts at 160°; its alcoholic solution shows a blue fluorescence. The *isonitroso*-derivative,



prepared by the action of amyl nitrite on the preceding compound, crystallises from benzene in yellow needles and melts and decomposes at 157—158°.

6:4'-*Dimethoxyflavonol*, $\text{OMe} \cdot \text{C}_6\text{H}_3 \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe} \\ | \\ \text{CO} \cdot \text{C} \cdot \text{OH} \end{array}$, prepared by

hydrolysing the preceding oxime, crystallises from alcohol in pale yellow needles and melts at 184—185°; it is insoluble in cold sodium hydroxide, but on warming forms a deep yellow, very sparingly soluble, sodium derivative. The *acetyl* derivative, $\text{C}_{19}\text{H}_{16}\text{O}_6$, crystallises from dilute alcohol in colourless, silky needles and melts at 131—132°.

6:4'-*Dihydroxyflavonol*, $\text{OH} \cdot \text{C}_6\text{H}_3 \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OH} \\ | \\ \text{CO} \cdot \text{C} \cdot \text{OH} \end{array}$, prepared by the

action of hydriodic acid on the dimethyl ether, crystallises from alcohol in bright yellow needles and melts and decomposes at 340°. The *triacetyl* derivative, $\text{C}_{21}\text{H}_{16}\text{O}_8$, crystallises from alcohol in rosettes of long, white needles and melts at 169°.

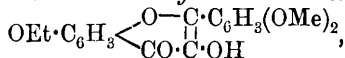
T. M. L.

Synthesis of Fisetin. STANISLAUS VON KOSTANECKI, VICTOR LAMPE, and JOSEF TAMBOR (*Ber.*, 1904, 37, 784—791).—7-*Ethoxy*-

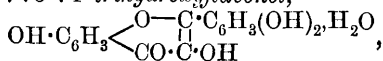
3':4'-dimethoxyflavanone, $\text{OEt} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} - \text{CH} \cdot \text{C}_6\text{H}_3(\text{OMe})_2 \\ | \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix}$, prepared by the action of 10 per cent. sulphuric acid on an alcoholic solution of 2'-hydroxy-4'-ethoxy-3:4-dimethoxychalkone,

$\text{OEt} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CO} \cdot \text{CH} : \text{CH} \cdot \text{C}_6\text{H}_3(\text{OMe})_2$, crystallises from alcohol in colourless, flat prisms, melts at 110° , and dissolves with an orange-yellow colour in alcoholic potassium hydroxide.

Its isonitroso-derivative, $\text{OEt} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} - \text{CH} \cdot \text{C}_6\text{H}_3(\text{OMe})_2 \\ | \\ \text{CO} \cdot \text{C} : \text{N} \cdot \text{OH} \end{smallmatrix}$, crystallises from benzene in pale yellow, almost colourless needles and melts and decomposes at $175-176^\circ$. 7-Ethoxy-3':4'-dimethoxyflavonol,



crystallises from much alcohol in bright yellow, glistening, broad needles and melts at $193-194^\circ$. Its acetyl derivative, $\text{C}_{21}\text{H}_{20}\text{O}_7$, crystallises from dilute alcohol in colourless needles and melts at $162-163^\circ$. The 7:3':4'-trihydroxyflavonol,



prepared by the action of hydriodic acid on the ethyl dimethyl ether, proved to be identical with fisetin, and gave the same tetra-acetyl derivative.

T. M. L.

Synthesis of 6:3'-Dihydroxyflavonol. STANISLAUS VON KOSTANECKI and ADOLF OTTMANN (*Ber.*, 1904, 37, 957-960).—6:3'-Dimethoxy-

flavanone, $\text{OMe} \cdot \text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} - \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe} \\ | \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix}$, prepared by the action of

sodium hydroxide on a mixture of quinacetophenone methyl ether and *m*-methoxybenzaldehyde, crystallises in colourless plates melting at 104° ; its alcoholic solution has a blue fluorescence, and it dissolves in concentrated sulphuric acid with an orange-red coloration. The isonitroso-derivative crystallises in yellow needles melting and decomposing at $153-154^\circ$; it produces a red shade with cobalt mordants and a yellow with uranium, cadmium, and lead mordants owing to the presence of the colouring complex, $\text{O} : \text{C} : \text{C} : \text{N} \cdot \text{OH}$.

6:3'-Dimethoxyflavonol, prepared by heating isonitrosodimethoxyflavanone dissolved in glacial acetic acid with dilute sulphuric acid, crystallises in light yellow, prismatic needles melting at 144° ; it is insoluble in cold dilute sodium hydroxide, but on warming, a deep yellow, sparingly soluble sodium salt is precipitated. It gives yellow shades with aluminium mordants. The acetyl derivative crystallises from dilute alcohol in long, white plates melting at 134° .

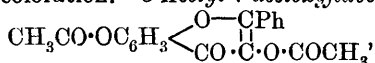
6:3'-Dihydroxyflavonol, $\text{OH} \cdot \text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} - \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OH} \\ | \\ \text{CO} \cdot \text{C} \cdot \text{OH} \end{smallmatrix}$, crystallises from

alcohol in bright yellow needles and melts and decomposes at 300° ; it gives bright yellow shades with aluminium and faint brown shades with iron mordants. The corresponding triacetyl derivative crystallises in colourless needles melting at $126-127^\circ$.

E. F. A.

Synthesis of 7-Hydroxyflavonol. STANISLAUS VON KOSTANECKI and M. L. STOPPANI (*Ber.*, 1904, 37, 1180—1182).—7-Methoxyflavanone, $\text{OMe} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} - \text{CHPh} \\ | \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix}$, prepared by the action of sulphuric acid on 2'-hydroxy-4-methoxychalkone (compare *Abstr.*, 1899, i, 368), crystallises in colourless needles melting at 91° , which dissolve in concentrated sulphuric acid with a greenish-yellow, and in alcoholic sodium hydroxide with an orange-yellow, coloration. The isonitroso-derivative crystallises in colourless plates melting and decomposing at 188° ; it gives orange shades with cobalt, and yellow shades with uranium mordants.

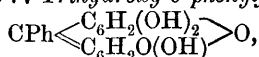
7-Methoxyflavonol, $\text{OMe} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} - \text{CPh} \\ | \\ \text{CO} \cdot \text{C} \cdot \text{OH} \end{smallmatrix}$, crystallises in long, colourless needles melting at 180° ; it is insoluble in dilute sodium hydroxide, but forms a yellow, sparingly soluble sodium derivative on heating; concentrated sulphuric acid gives rise to a faint yellow coloration and blue fluorescence; with aluminium mordants, bright yellow tints are produced. The acetyl derivative forms colourless needles grouped in rosettes, which melt at 140° . 7-Hydroxyflavonol crystallises in faintly yellow, almost colourless, prismatic needles, which melt at $257\text{--}259^\circ$ and are easily soluble in dilute sodium hydroxide with a greenish-yellowish coloration. 3-Acetyl-7-acetoxyflavonol,



forms large, colourless needles which melt at 157° .

E. F. A.

Condensation of Hydroxyquinol with Aldehydes. CARL LIEBERMANN and S. LINDENBAUM [and, in part, A. GLAWE] (*Ber.*, 1904, 37, 1171—1180).—2:3:7-Trihydroxy-9-phenylfluorone,



prepared by the condensation of benzaldehyde with hydroxyquinol, is an orange-red, crystalline substance very sparingly soluble in organic solvents; the alcoholic solution has a greenish-yellow fluorescence. It dissolves in alkali with a carmine-red coloration, the potassium salt dissolves with a purple coloration in water. It gives orange-red shades with aluminium and greyish-violet with iron mordants; the sulphate, $\text{C}_{19}\text{H}_{12}\text{O}_5 \cdot \text{H}_2\text{SO}_4$, crystallises with a molecule of ethyl acetate forming gold, glistening platelets. 2:3:7-Triacetoxy-9-phenylfluorone crystallises in orange-yellow needles melting at $230\text{--}233^\circ$. Hydroxyquinol condenses with formaldehyde yielding methylenebis-hydroxyquinol, $\text{CH}_2[\text{C}_6\text{H}_2(\text{OH})_3]_2$, which crystallises in silvery, glistening needles melting at $227\text{--}230^\circ$, and forming an acetate, $\text{C}_{13}\text{H}_6\text{O}_6\text{Ac}_6$, which crystallises in colourless, glistening prisms and melts at $152\text{--}155^\circ$.

2:3:7-Trihydroxy-9-methylfluorone, $\text{CMe} \begin{smallmatrix} \text{C}_6\text{H}_2(\text{OH})_2 \\ | \\ \text{C}_6\text{H}_2\text{O}(\text{OH}) \end{smallmatrix} \text{O}$, produced by condensing hydroxyquinol with para-aldehyde in presence of sulphuric acid, is a red powder sparingly soluble in water; the alcoholic solution and also that in concentrated sulphuric acid are yellow,

and have a yellowish-green fluorescence. With the ordinary oxidising mordants, yellow shades are produced.

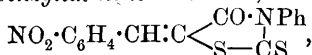
Colourless condensation products are produced by the condensation of benzaldehyde with pyrogallol, resorcinol, or phloroglucinol.

E. F. A.

Substituted Rhodanic Acids and their Aldehyde Condensation Products. II. RUDOLF ANDREASCH and ARTHUR ZIPSER (*Monatsh.*, 1904, 25, 159—180. Compare Abstr., 1903, i, 855).—

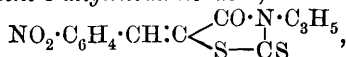
3-Phenylrhodanic acid is most conveniently prepared by von Braun's method (Abstr., 1903, i, 13). Boiling with alkali or barium hydroxide hydrolyses it, forming diphenylthiocarbamide and thioglycollic acid: $2C_6H_7ONS_2 + 4H_2O = 2C_2H_4O_2S + H_2S + CO_2 + CS(NHPh)_2$.

3-Phenyl-5-m-nitrobenzylidenerhodanic acid,



from phenylrhodanic acid and *m*-nitrobenzaldehyde, crystallises from alcohol in bright yellow scales with faint blue reflex, melts at 240° (uncorr.), and dissolves readily in acetone, hot alcohol, or ether, sparingly in glacial acetic acid.

5-m-Nitrobenzylidene-3-allylrhodanic acid,

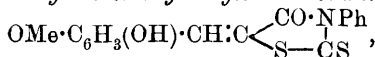


crystallises in yellow, microscopic plates and melts at 145°.

3-Phenyl-5-p-nitrobenzylidenerhodanic acid forms small, yellow needles dissolving very sparingly in cold acetone, more readily on warming, and blackens at 240° without melting.

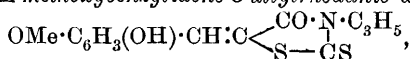
5-p-Nitrobenzylidene-3-allylrhodanic acid forms golden-yellow scales and melts at 153°.

3-Phenyl-5-p-hydroxy-m-methoxybenzylidenerhodanic acid,



from phenylrhodanic acid and vanillin, crystallises in very slender, yellow needles and melts at 193°.

5-p-Hydroxy-m-methoxybenzylidene-3-allylrhodanic acid,



forms spherical aggregates of orange needles and melts at 146°.

3-Phenyl-5-o-hydroxybenzylidenerhodanic acid,



from salicylaldehyde, crystallises in chrome-yellow needles, melts at 172°, and dissolves in alkalis to red solutions. The *acetyl* derivative crystallises from alcohol in white needles and melts at 202°.

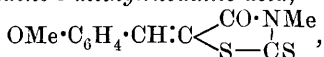
3-Methylrhodanic acid, $CH_2 \begin{array}{l} \text{CO} \cdot NMe \\ \text{S} - CS \end{array}$, prepared by heating a solu-

tion of methylthiocarbimide and thioglycollic acid in dilute alcohol, crystallises from water in slender, white needles and melts at 72°.

It is neutral and is isomeric with the 5-methylrhodanic acid prepared by Berlinerblau (Abstr., 1886, 326).

5-Benzylidene-3-methylrhodanic acid, from benzaldehyde and 3-methylrhodanic acid, crystallises from alcohol in woolly, sulphur-yellow needles and melts at 169°.

5-p-Methoxybenzylidene-3-methylrhodanic acid,



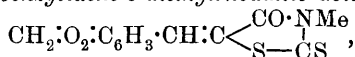
from anisaldehyde, forms felted, golden-yellow needles and melts at 181°.

5-m-Nitrobenzylidene-3-methylrhodanic acid forms greenish-yellow needles and melts at 233°.

5-p-Nitrobenzylidene-3-methylrhodanic acid forms orange scales and melts at 205°.

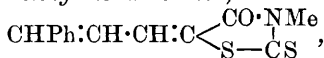
5-p-Hydroxy-m-methoxybenzylidene-3-methylrhodanic acid, from vanillin and 3-methylrhodanic acid, forms orange needles and melts at 199°.

5-Methylenedioxybenzylidene-3-methylrhodanic acid,



from piperonal, forms microscopic, yellow needles and melts at 204°.

5-Cinnamylidene-3-methylrhodanic acid,



forms dark orange-coloured needles and melts at 226°.

3-Ethylrhodanic acid, $\text{CH}_2 \begin{array}{l} \text{CO} \cdot \text{NEt} \\ \text{S} - \text{CS} \end{array}$, prepared from thioglycollic acid and ethylthiocarbimide, is an uncrystallisable oil, but yields highly-crystalline condensation products.

5-Benzylidene-3-ethylrhodanic acid crystallises from 70 per cent. alcohol in flat, glistening, greenish-yellow needles and melts at 149°.

5-o-Hydroxybenzylidene-3-ethylrhodanic acid forms orange needles with blue reflex and melts at 190°.

5-p-Methoxybenzylidene-3-ethylrhodanic acid, forms felted, yellow needles and melts at 143°.

5-m-Nitrobenzylidene-3-ethylrhodanic acid forms glistening, greenish-yellow leaflets or flat needles and melts at 188°.

5-p-Hydroxy-m-methoxybenzylidene-3-ethylrhodanic acid forms felted, yellow needles and melts at 140°.

5-Methylenedioxybenzylidene-3-ethylrhodanic acid forms woolly, yellow needles and melts at 154°.

5-Cinnamylidene-3-ethylrhodanic acid forms yellow scales and melts at 187°.

3-Phenyl-5-methylrhodanic acid, $\text{CHMe} \begin{array}{l} \text{CO} \cdot \text{NPh} \\ \text{S} - \text{CS} \end{array}$, prepared by boiling phenylthiocarbimide and α -thiolactic acid in dilute alcohol or by boiling an alcoholic solution of ammonium phenyldithiocarbamate and ethyl α -bromopropionate, crystallises from alcohol in thin, greenish-white plates, melts at 118–119°, and does not form condensation products with aldehydes.

C. H. D.

Methods for obtaining Organic Bases from Vegetable Juices and Extracts. ERNST SCHULZE (*Landw. Versuchs-Stat.*, 1904, 59, 344—354. Compare Abstr., 1895, ii, 364).—The following method is employed for the isolation of hexone bases. The extract, after precipitation with lead acetate, or tannic acid and lead acetate, is treated with phosphotungstic acid, and the precipitate rubbed with an excess of pure barium hydroxide and cold water. If any odour of ammonia is noticed, the ammonia is removed by passing air through the cold liquid. The filtered solution is then treated with carbon dioxide, exactly neutralised with nitric acid, and evaporated to a small volume, a little nitric acid being added from time to time to maintain neutrality. It is then precipitated with silver nitrate and filtered. More silver nitrate is added to the filtrate, until a drop of the solution gives a brownish-yellow precipitate with baryta water. Then the histidine and arginine are successively precipitated (as silver compounds) by baryta (Kossel and Kutscher, *Zeit. physiol. Chem.*, 31, 170—175). The arginine-silver precipitate is purified by Kossel's method. The histidine precipitate is treated with dilute hydrochloric acid, filtered, and precipitated with phosphotungstic acid. The precipitate is decomposed with baryta, the filtrate treated with carbon dioxide, and the histidine precipitated with mercuric chloride. The product is finally treated with hydrogen sulphide. The precipitation with mercuric chloride is not complete, and involves loss of substance, but the method yields a pure product.

The filtrate from the arginine silver compound is neutralised with hydrochloric acid and evaporated down. After removing the inorganic salts as far as possible, the residue is extracted with hot absolute alcohol, which dissolves the hydrochlorides of choline, betaine, trigonelline, stachydrine, and guanidine, leaving a residue which may contain lysine. The further separation of the bases is effected by means of the mercurichlorides and platinichlorides. N. H. J. M.

Mutual Solubility of Nicotine and Water. C. S. HUDSON (*Zeit. physikal. Chem.*, 1904, 47, 113—115).—Nicotine and water are miscible in all proportions at temperatures below 60° and above 210°. At temperatures between 60° and 210°, the miscibility is limited, except when one of the components is in very large excess. Above 90°, a saturated solution of water in nicotine is lighter than a saturated solution of nicotine in water; below 90°, the reverse is the case. When nicotine is mixed with water, much heat is developed, probably owing to the formation of a hydrate. The marked variation of the rotation and of the refraction with the concentration points to the same interpretation. To the presence of such a hydrate the miscibility of the two otherwise immiscible liquids, nicotine and water, may be attributed. J. C. P.

Action of Bromine on Strychnine. LÉON MARTIN (*Bull. Soc. Chim.*, 1904, iii, 31, 386—391).—*Bromostrychnine*, $C_{21}H_{21}O_2N_2Br$, prepared by the addition of bromine dissolved in hydrobromic acid (50 per cent.) to an aqueous solution of strychnine hydrobromide in presence of hydrobromic acid and sodium acetate until the orange-

yellow precipitate formed on each addition of the reagent begins to be permanent, crystallises from warm alcohol on diluting with water in colourless needles and melts at 199° . The *methiodide* forms slightly yellow needles and melts at 298° ; the *ethiodide* melts at 272° .

When the liquid in which bromostyrychnine has been produced is poured into excess of the brominating mixture, *bromostyrychnine bromide hydrobromide*, $C_{21}H_{21}O_2N_2Br, Br, HBr$, is formed; this is a crystalline, yellow powder, which melts at 204° and dissolves in neutral solvents with the liberation of one atom of bromine; the latter is also removed by sodium thiosulphate. The substance becomes resinous on exposure to light.

Dibromostyrychnine, produced by brominating bromostyrychnine at 100° , forms small crystals, which become coloured on exposure to light; it melts at $130-131^{\circ}$ and is soluble in alcohol. The *methiodide* melts at 243° and the *ethiodide* at 251° .

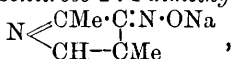
Dibromostyrychnine bromide hydrobromide, prepared from the foregoing, like the analogous monobromo-compound forms microscopic, yellow crystals and melts at 146° . On exposure to light or heat it becomes resinous.

Iodostrychnine iodide hydriodide, prepared by the addition of hydrobromic acid to a boiling solution of strychnine in dilute iodic and sulphuric acids, is a brown substance which melts at 154° , and when treated with acetone and subsequently with ammonia solution furnishes *iodostyrychnine*; this is a maroon-coloured, crystalline powder which melts at 188° .

Strychnine di-iodide, $C_{21}H_{22}O_2N_2I_2$, obtained by the action of iodine (2 atoms) on the alkaloid (1 mol.) in the presence of sodium acetate and hydriodic acid, forms ruby-red crystals, dissolves partially in organic solvents with the liberation of iodine, and melts with decomposition.

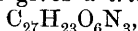
T. A. H.

Transformations of the Nitrosopyrroles. FRANCESCO ANGELICO and ENRICO CALVELLO (*Gazzetta*, 1904, 34, i, 38--50. Compare this vol., i, 188).—*Sodium 3-isonitroso-2:4-dimethylpyrrole*,



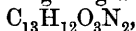
prepared by the action of amyl nitrite on an alcoholic solution of pyrrole containing sodium ethoxide, forms reddish-yellow crystals; when it is decomposed by dilute sulphuric acid, and extracted with ether, a beautiful, transitory green colour is imparted to the solvent, showing the formation of the true nitroso-compound, $\text{NH} \leq \begin{array}{c} \text{CMe} \cdot \text{C} : \text{NO} \\ | \\ \text{CH} = \text{CMe} \end{array}$.

Sodium 3-isonitroso-2:5-dimethylpyrrole was also prepared; it is decomposed by a cold alkaline solution of hydroxylamine giving the *trioxime*, $\text{OH} \cdot \text{N} : \text{CMe} \cdot \text{C} (\text{N} \cdot \text{OH}) \cdot \text{CH}_2 \cdot \text{CMe} \cdot \text{N} \cdot \text{OH}$, of a *hexane-βγε-trione*, which separates from alcohol in magnificent white crystals, melts at 159° , and gives a *tribenzoyl* derivative,



decomposing at 180° . On warming the trioxime with dilute sulphuric acid, a *substance*, $C_6H_8O_2N_2$, is obtained by the loss of hydroxylamine,

crystallising from light petroleum in needles and melting at 117° ; several formulæ may be given to the substance. That it contains a hydroxyl group is shown by its giving a *benzoyl* derivative,



which crystallises from benzene in minute needles and melts at 180 – 181° ; with phenylcarbimide, the compound $\text{C}_{13}\text{H}_{13}\text{O}_3\text{N}_3$ is formed, melting at 178 – 180° . The final action of sulphuric acid on the

trioxime is to form a substance $\text{C}_6\text{H}_7\text{O}_2\text{N}$, probably $\text{CH} \begin{smallmatrix} \text{CMe} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{CAc} \cdot \text{N} \end{smallmatrix}$ or

$\text{CH} \begin{smallmatrix} \text{CMe} \cdot \text{N} \\ \diagup \quad \diagdown \\ \text{CAc} \cdot \text{O} \end{smallmatrix}$, which crystallises in nacreous leaflets, melts at 22° ,

boils at 177° , and with iodine and aqueous potassium hydroxide gives rise to iodoform; the *p*-nitrophenyllhydrazone, $\text{C}_{12}\text{H}_{12}\text{O}_3\text{N}_4$, crystallises from alcohol in lustrous, yellow needles and melts and decomposes at 235° .

W. A. D.

Dinitrophenylpyridinium Chloride and its Products of Change. THEODOR ZINCKE (*Annalen*, 1904, 330, 361–374).—

1-Chloro-2:4-dinitrobenzene reacts with pyridine giving the chloride of the ammonium base, $\text{C}_5\text{H}_5\text{NCl} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2$, which reacts with alkali hydroxides in the following manner: if the aqueous solution is made alkaline, a brownish-red precipitate separates and a violet solution is formed; on now adding acid to the whole, a brilliant red precipitate is formed. This material is also produced when an alkali hydroxide is added drop by drop to the acid solution, the solution never becoming permanently alkaline. This substance appears possibly

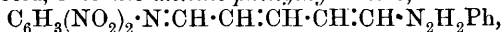
to be the *pseudo-base*, $\text{CH} \begin{smallmatrix} \text{CH}=\text{CH} \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{CH}(\text{OH}) \end{smallmatrix} \text{N} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2$, as it dis-

solves in alkali hydroxides and is changed, although but slowly, back into the ammonium base (compare Spiegel, *Abstr.*, 1900, i, 51; 1901, i, 752; Vongerichten, *Abstr.*, 1900, i, 51; Reitzenstein, *Abstr.*, 1903, i, 815). The red substance is nearly quantitatively converted into the ammonium base, when it is heated with an acetic acid solution of hydrogen chloride, but when the red compound is treated with aqueous hydrochloric acid, 2:4-dinitroaniline is formed, a fact which favours the view that the red substance is represented by the formula $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{N} : \text{CH} : \text{CH} : \text{CH} : \text{CH}_2 \cdot \text{CHO}$; all attempts to isolate the corresponding dialdehyde together with the dinitroaniline in the action of hydrochloric acid failed. It has, however, been obtained in the form of a dianilide, $\text{NPh} : \text{CH} : \text{CH} : \text{CH} : \text{CH} : \text{NHPh}$, when the red substance or the tertiary ammonium salt is allowed to interact with aniline; from the ammonium salt, dinitroaniline is formed at the same time; the free *base* crystallises in orange-yellow leaflets and the *hydrochloride* in red needles. When boiled with hydrochloric acid or heated for a short time at its melting point, the hydrochloride of the dianilide is decomposed into aniline and *phenylpyridinium chloride*, the pyridine ring being again regenerated. This tertiary ammonium salt can be directly prepared from the dinitrophenylpyridinium chloride by heating it with aniline at 100° for a considerable time.

When the dianilide is treated with excess of bromine, it is con-

verted into *s*-tribromoaniline and the *perbromide* of *s*-tribromophenylpyridinium bromide, $C_5H_5NBr_3 \cdot C_6H_2Br_3$, which is not affected by aniline.

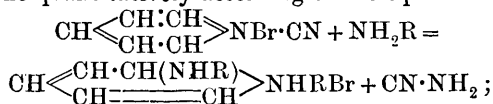
Both the dinitroammonium salt and the red substance obtained from it by the action of alkalis are converted by phenylhydrazine, even in the cold, into the *anilino-phenylhydrazide*,



which crystallises in lustrous, black needles.

It is noteworthy that the dianilide and anilino-phenylhydrazide are intensely coloured, a property which appears to depend on the unsaturated carbon chain, since Claisen (this vol., i, 14) found that the dianilide of propargylaldehyde is coloured. K. J. P. O.

A New Class of Colouring Matters derived from Pyridine. W. KÖNIG (*J. pr. Chem.*, 1904, [ii], 69, 105—137).—When pyridine is mixed with cyanogen bromide in ethereal solution, and a primary aromatic amine is then added, it seems that the pyridine and cyanogen bromide first form an additive product, which then reacts with the amine quantitatively according to the equation



cyanamide remains in solution, whilst the *arylaminoaryldihydropyridinium bromide* is precipitated. This has a colour varying from red to blue, and crystallises well from acetic acid, alcohol, &c.; it dyes fabrics of animal origin, and also vegetable fabrics to some extent, but the dyed fabrics will not bear washing. When the colouring matter is heated with concentrated hydrochloric acid at 160° for several hours, it is hydrolysed to the amine, NH_2R , and an *arylpyridinium chloride*, $CH \begin{array}{c} \swarrow CH:CH \\ \searrow CH:CH \end{array} NRCl$. The corresponding base separates in an impure state when the solution is made alkaline; it is best purified by dissolving it in hydrochloric acid and adding the solution to a concentrated solution of ferric chloride, when a compound with $1FeCl_3$ separates, which can be purified by crystallisation from acetic acid. From the solution of this compound, the iron can be precipitated with sodium hydroxide, and other salts may be prepared from the remaining solution by the addition of suitable acids. The phenyl colouring matter ($R = Ph$) yields aniline and a little pyridine when distilled; bromine does not simply brominate it, but decomposes it into tribromoaniline and phenylpyridinium bromide.

The colouring matters may also be prepared from a solution of pyridine and the amine in an acid, and instead of pure cyanogen bromide the aqueous solution of that substance obtained in its preparation may be used; it is usually necessary to add an alkali in order to get the colouring matter formed. In the case of an amino-acid, the sodium salt may be used suitably. The pure base can be precipitated with alcoholic ammonia from the solution of its chloride in alcohol, and from it, salts with other acids can be prepared. Some of these colouring matters crystallise from different solvents in forms

which appear quite different; these may perhaps be examples of stereoisomeric derivatives of quinquevalent nitrogen. That one of the residues in the amine enters the 2 or 6 position in the pyridine ring is apparent from the fact that 2-methylpyridine (picoline) yields a colouring matter, but 2:4:6-trimethylpyridine (collidine) does not. In one case (methylaniline), a colouring matter was obtained from a secondary amine, which was soluble in hot water, although not in cold. The formation of a colouring matter from pyridine, a primary amine, and cyanogen bromide may be used as a test for either of these substances. The following substances were prepared and analysed; the temperatures are melting points.

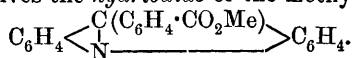
Arylaminoaryldihydropyridinium Bromides.—From aniline, $R = Ph$, 162° ; *m*-xylylidine, $R = C_6H_3Me_2$, 153° ; ψ -cumidine, $R = 1:3:4-C_6H_2Me_3$, 158° ; the naphthylamines, $R = C_{10}H_7$; β , 182° ; α , 158° ; *p*-phenetidine, $R = C_6H_4 \cdot OEt$, 143° ; *p*-aminophenol, $R = C_6H_4 \cdot OH$, 181° ; sodium sulphanilate, $R = C_6H_4 \cdot SO_3Na$ and $(NH) \langle \underset{O}{\underset{|}{C_6H_4}} \rangle SO_2$; aminoazobenzene, $R = C_6H_4 \cdot N:NPh$, 159° ; methylaniline, $NHR = NMePh$, 139° . From 2-methylpyridine (picoline) and *o*-toluidine, 143° .

Arylpyridinium Salts.—From aniline, $R = Ph$; *ferrichloride*, 158° ; *platinichloride*, 206° (decomposes); *aurichloride*, 182° ; *dichromate*, 123° ; *ferrichloride* of the *bromide*, 123° . From the naphthylamines: β : *ferrichloride*, 130° ; *platinichloride*, 194° (with decomposition); *aurichloride*, 203° ; *iodide*, 201° ; α : *ferrichloride*, $119-120^\circ$; *picrate*, $192-193^\circ$.
C. F. B.

Preparation of Indole from Indoxyl. DANIEL VORLÄNDER and O. APALT (*Ber.*, 1904, 37, 1134—1135).—A good yield of indole is obtained by reducing indoxyl or indoxylic acid in alkaline solution with sodium amalgam or zinc dust. The best material is the product obtained by fusing indoxylic acid with sodium hydroxide. The mixture is distilled with steam, when a part of the indoxyl condenses in crystalline form, and the remainder may be precipitated as the picrate.

1-Methylindole is obtained in similar manner from 1-methylindoxylic acid.
C. H. D.

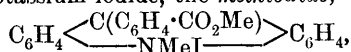
Ammonium Compounds. Methylation of 5-Phenylacridine-*o*-carboxylic Acid. HERMAN DECKER and THEODOR HOCK (*Ber.*, 1904, 37, 1002—1012. Compare *Abstr.*, 1903, i, 518).—When 5-phenylacridine-*o*-carboxylic acid, $C_6H_4 \langle \underset{N}{\underset{|}{C(C_6H_4 \cdot CO_2H)}} \rangle C_6H_4$ (Bernthsen, *Abstr.*, 1884, 1356), is heated with methyl iodide for 4 hours at 120° , it gives the *hydriodide* of the methyl ester,



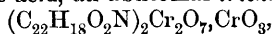
The *methyl* ester itself is obtained by substituting the sodium salt for the free acid, or by heating the acid with methyl alcohol containing hydrogen chloride; it crystallises from xylene in bright yellow needles and melts at 173° . The *hydriodide* forms dark-red, fan-shaped aggregates of crystals and melts at $228-230^\circ$; the *picrate*,

$C_{27}H_{18}O_9N_4$, melts at 241° and the *dichromate* crystallises with $1H_2O$, and melts when anhydrous at 147° .

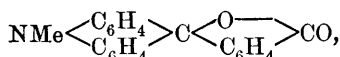
On heating the methyl ester with methyl sulphate for 2 hours at 120° and adding potassium iodide, the *methiodide*,



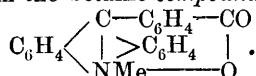
is obtained; it crystallises in garnet coloured needles and melts at $226-227^\circ$. The *picrate*, $C_{26}H_{18}O_9N_4$, of the *N*-methyl derivative, melts at 201° ; with chromic acid, an abnormal *trichromate*,



is obtained, crystallising in small, orange coloured cubes. When any one of these esters is decomposed by cold aqueous sodium hydroxide, the *lactone*,



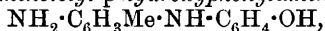
of 5-hydroxy-5-phenyl-10-methylidihydroacridinecarboxylic acid is obtained; it crystallises from benzene or xylene in white leaflets or cubes, melts at 245° , sublimes unchanged, and dissolves in acids giving salts derived from the betaine compound,



Thus, on dissolving it in hydrochloric acid and adding potassium iodide, the *iodide*, $C_6H_4 \left\langle \begin{array}{c} C(C_6H_4 \cdot CO_2H) \\ NMeI \end{array} \right\rangle C_6H_4$, is formed, which crystallises from water with $1H_2O$; the corresponding *picrate*, $C_{27}H_{18}O_9N_4$, crystallises from alcohol in large, lustrous, yellow prisms and melts at $212-215^\circ$; the *dichromate* is an orange-red, crystalline powder melting at $252-255^\circ$. W. A. D.

Some Amino- and Aminohydroxy-diphenylamines. ROBERT GNEHM [with H. BOTS] (*J. pr. Chem.*, 1904, [ii], 69, 161-175).—A detailed description is given of the preparation of *p*-dimethylamino-*p*-hydroxydiphenylamine and some of its derivatives (compare Abstr., 1902, i, 831). When the base is heated for 24 hours at 110° with a solution of sulphur in concentrated aqueous sodium sulphide, the leuco-derivative of a blue *colouring matter*, $C_{14}H_{12}O_2N_2S_3$, is formed; it can be oxidised to the latter by aspirating air through its alkaline solution. The *colouring matter* is soluble in alkali hydroxides and in concentrated, although not in dilute, acids; an amorphous zinc salt, $C_{14}H_{10}O_2N_2S_3 \cdot Zn$, a crystalline sodium hydrogen sulphite compound, $C_{14}H_{12}O_2N_2S_3 \cdot NaHSO_3 \cdot 2H_2O$, and an amorphous *diacetyl* derivative were prepared and analysed.

When a solution of *p*-aminophenol and *o*-toluidine in dilute sulphuric acid is oxidised with sodium dichromate, a *colouring matter* is formed; addition of sodium sulphide then effects a reduction to the leuco-derivative, *p*-aminotolyl-*p*-hydroxyphenylamine,



which can be crystallised from water; it melts at $159-160^\circ$.

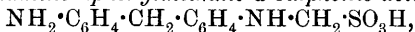
A blue *colouring matter* is formed when molecular proportions of dimethyl-*p*-phenylenediaminethiosulphonic acid and phenol, dissolved

in dilute aqueous sodium carbonate, are oxidised at 0° with 2 per cent. aqueous sodium hypochlorite; the sodium salt can be salted out with sodium chloride, and can be reduced to the leuco-derivative by means of hydrogen sulphide, but neither substance was obtained pure.

C. F. B.

Methyldiaminodiarylmethane- ω -sulphonic Acids. ANILIN-FARBEN- & EXTRACT-FABRIKEN VORM JOH. RUD. GEIGY (D.R.-P. 148760).—Aromatic amino-compounds in which either an ortho- or a para-position is unoccupied react with formaldehyde and sulphurous acid, slowly at the ordinary temperature, rapidly at 70–90°, forming methyldiaminodiarylmethane- ω -sulphonic acids, which are diazotisable, and are readily hydrolysed to diaminodiarylmethane, formaldehyde, and alkali sulphite.

Methyl-4 : 4'-diaminodiphenylmethane- ω -sulphonic acid,



from aniline, formaldehyde, and sulphurous acid, is a white powder, melting and decomposing at 168°. The ammonium salt forms silvery needles and dissolves readily in water. 3 : 3'-Dichloromethyl-4 : 4'-diaminodiphenylmethane- ω -sulphonic acid, from *o*-chloroaniline, melts at 168–169°. *Methyl-4 : 4'-diamino-3 : 3'-ditolylmethane- ω -sulphonic acid*, from *o*-toluidine, is an almost insoluble powder, melting at 172°. *Methyl-4 : 4'-diamino-2 : 2'-ditolylmethane- ω -sulphonic acid*, from *m*-toluidine, melts at 178–180°. *Methyl-2 : 2'-diamino-3 : 3'-ditolylmethane- ω -sulphonic acid*, from *p*-toluidine, melts at 159–160°. *Methyl-4 : 4'-diaminodixylylmethane- ω -sulphonic acid* melts at 170° and forms a sparingly soluble ammonium salt. *Methyldiaminodinaphthylmethane- ω -sulphonic acid*, from α -naphthylamine, is crystalline and melts at 193–195°.

C. H. D.

Action of Phosphorus Pentachloride on Trisubstituted Carbamides. A. STEINDORFF (*Ber.*, 1904, 37, 963–966).—*Triphenylchloroamidine*, prepared by the action of phosphorus pentachloride on triphenylcarbamide at 120°, distils at 240–250° under 24 mm. pressure, and forms colourless crystals, melting at 90–92°. It reacts with aniline, forming *tetraphenylguanidine*, which melts at 137–140°, and yields a *platinichloride* melting at 240–242°; with diphenylamine, it gives *pentaphenylguanidine*, melting at 177–179°.

Ethylisotriphenylcarbamide, prepared by the action of sodium and alcohol on the amidine, boils at 210–220° under 35 mm. pressure and melts at 48–50°; its *platinichloride* melts at 81–83°. *isoTetraphenylthiocarbamide*, prepared by the action of sodium and thiophenol in alcoholic solution on the amidine, melts at 185–188°, is soluble in concentrated acids, and forms a *platinichloride* melting at 135–138°.

Diphenyltolylchloroamidine distils at 240–250° under 30 mm. pressure, and melts at 105–107°; it is prepared and reacts with bases in a similar manner to the triphenylchloroamidine.

E. F. A.

Benzidine Transformation. J. POTTER VAN LOON (*Rec. trav. chim.*, 1904, 23, 62–97. Compare *Abstr.*, 1903, i, 249).—The author has investigated the respective influences of the various factors in the con-

version of hydrazobenzene into benzidine by the action of acids. The amount of benzidine formed at first increases with the concentration of the acid and ultimately decreases with this; it is independent of the nature of the acid, and diminishes (1) as water is replaced by methyl or ethyl alcohol as a solvent and (2) as the temperature is increased. Tables illustrating these statements are given in the original. At 100°, hydrazobenzene is partially decomposed into azobenzene and aniline.

Determinations of the velocity of the transformation into benzidine were made under various conditions. Using 50 per cent. alcohol and normal hydrochloric acid, the value of k was found to be 0.345 to 0.391; with 15 per cent. alcohol and with $N/10$, $N/20$ and $N/40$ hydrochloric acid, the values of k found were respectively 0.213 to 0.238, 0.296 to 0.310, and 0.383 to 0.500. The foregoing determinations were made at 25°; with $N/20$ acid and 15 per cent. alcohol at 30.2°, the value of k was 0.520 to 0.557. The variations in the value of k for each concentration of acid are regarded as due to secondary hydrolysis, and the variations in this constant for different concentrations of acid, it is suggested, may be due to the concentration of hydrazobenzene not remaining constant, in spite of precautions taken to ensure this, during the experiments.

The value of k for nitric acid is similar to that found for hydrochloric acid under the same conditions, and that for dichloroacetic acid has about one-fourth this value. These results indicate that the transformation is due solely to the hydrogen ions of the acid. T. A. H.

Conversion of Derivatives of Hydrazine into Heterocyclic Compounds. ROBERT STOLLÉ (*J. pr. Chem.*, 1904, [ii], 69, 145—160. Compare *ibid.*, 68, 130).—A detailed description of experiments that have been described briefly already (Abstr., 1899, i, 413, 456).

Tribenzoylhydrazine, $\text{CPhO} \cdot \text{NBz} \cdot \text{NHBz}$ or $\text{OBz} \cdot \text{CPh} : \text{N} \cdot \text{NHBz}$, appears to be described for the first time. It is obtained from benzoyl chloride and dibenzoylhydrazine in the presence of pyridine, or from benzoyl chloride and sodiodibenzoylhydrazine, or by boiling azodibenzoyl with water or dilute alcohol; it melts at 212°, and decomposes into diphenylfurodiazole and benzoic acid when maintained at 200°.

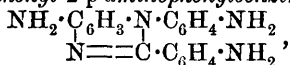
From benzoyl chloride and dibenzoylhydrazine, in benzene solution in the presence of pyridine, Weindel has obtained a second tribenzoylhydrazine, melting at 198°; the two substances are perhaps the tautomeric modifications. C. F. B.

[Ethyl Phenylsemicarbazide- α -carboxylate.] A Correction. SALOMON F. ACREE (*Ber.*, 1904, 37, 995. Compare *ibid.*, 622).—The statement previously made that an ethyl ester was formed by the interaction of silver phenylsemicarbazide- α -carboxylate and ethyl iodide is incorrect; the silver salt used contained a small quantity of the ester as impurity. E. F. A.

Benziminazoles and Dyes derived from them. OTTO KYM (*Ber.*, 1904, 37, 1070—1074).—*opp'-Trinitrotribenzoyl-triaminodiphenylamine*, $\text{C}_{33}\text{H}_{23}\text{O}_9\text{N}_7 \cdot \text{H}_2\text{O}$, prepared by the Schotten-Baumann method, crystallises from acetic acid and water in yellowish-green, glistening flakes, melts at 180—190°, becomes solid on further heating, and again

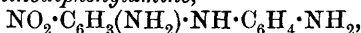
melts at 303—304°; it is very sparingly soluble in all solvents except nitrobenzene, from which it separates in minute, yellow, anhydrous needles.

5-Amino-1-p-aminophenyl-2-p-aminophenylbenziminazole,



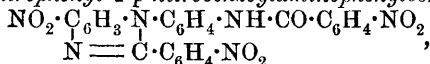
prepared by energetic reduction of the preceding compound with tin and hydrochloric acid, crystallises from dilute alcohol in minute, greyish-white needles and melts at 223—224°.

p-Nitro-o-p'-diaminodiphenylamine,



prepared by reducing dinitroaminodiphenylamine with sodium sulphide, crystallises from alcohol in long, reddish-black needles with a metallic lustre, and melts at 188—189°.

5-Nitro-2-p-nitrophenyl-1-p-nitrobenzoylaminophenylbenziminazole,



prepared by heating the preceding compound at 180—200° with p-nitrobenzoyl chloride, crystallises from acetic acid in minute, heavy, yellow crystals, melts at 299—300°, and is reduced by tin and hydrochloric acid to the iminazole base just described; the yield of the base is, however, not large.

When diazotised and coupled with naphtholsulphonic acid, the iminazole base does not give deeper shades than the mono- and di-amino-compounds, but, on the contrary, the shade is distinctly redder. Neither do the second and third amino-groups increase the affinity of the diazo-dye for the cotton fibre or the depth of colour that can be produced, and it would therefore appear that the presence of a free (undiazotised) amino-group has little influence on this property. T. M. L.

[Precipitation of Rosaniline Solutions by Alkali.] HUGO WEIL (*Ber.*, 1904, 37, 1014—1015).—A reply to Jennings (*Ber.*, 1903, 36, 4022). W. A. D.

Colour Bases of the Triphenylmethane Dyes. ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1904, 37, 1183—1184. Compare *Abstr.*, 1902, i, 112, 355; 1903, i, 811, this vol., i, 308).—The aniline-blue corresponding with triphenylrosaniline, when acted on by alkali-hydroxides, yields not the colourless carbinol, but a black *phenylimide*, $\text{C}_{37}\text{H}_{29}\text{N}_3$, which behaves in a similar manner to the phenylimide of monoaminotriphenylcarbinol (*loc. cit.*). Paramagenta, when powdered with sodium hydroxide, yields quantitatively a polymeride of the *imide*, $\text{C}_{19}\text{H}_{17}\text{N}_3$, crystallising from xylene in almost colourless needles. The authors propose to discuss these observations at a later date.

E. F. A.

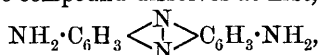
Preparation of Formyl-4:5-diamino-2:6-dihydroxy-1:3-dimethylpyrimidine. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D. R.-P. 148208).—Formyl-4:5-diamino-2:6-dihydroxy-1:3-dimethylpyrimidine (Traube, *Abstr.*, 1900, i, 416) may be prepared by methylating the formyl derivatives of 4:5-diamino-2:6-dihydroxypyrimidine

or 4 : 5-diamino-2 : 6-dihydroxy-3-methylpyrimidine by means of methyl iodide or methyl chloride at 30—40°. The presence of an excess of alkali must be avoided, or theophylline will be formed (Abstr., 1903, i, 527). C. H. D.

Preparation of Azine Compounds. KALLE & Co. (D.R.-P. 148113).—Sodium sulphide reduces the trinitrodiphenylamine,



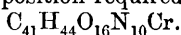
prepared from 1-chloro-2 : 4-dinitrobenzene and *m*-nitroaniline, on warming. The nitro-compound dissolves at first, and an *azine*,



separates in reddish-bronze needles or leaflets. Alcoholic or ethereal solutions of the azine show an orange fluorescence. Acids form three series of salts, green, red, and blue; reducing agents decolorise these solutions, the leuco-compound dissolves in ether to a fluorescent solution and oxidises in air.

Similar azines are obtained from such trinitro- or polynitro-diphenylamines as contain at least one nitro-group in the *ortho*- and another in the *meta*-position to the imino-group. Thus the trinitrophenyltolylamine prepared from 1-chloro-2 : 4-dinitrobenzene and 2-nitro-4-aminotoluene yields a *eurhodine*, resembling the above compound, but yellower in colour. C. H. D.

Action of Chromic Acid on Diphenylcarbazide. A. MOULIN (*Bull. Soc. chim.*, 1904, [iii], 31, 296—300. Compare Cazeneuve, Abstr., 1901, i, 655).—When diphenylcarbazide, dissolved in a mixture of alcohol (90°) with 10 per cent. of acetic acid, is added to chromic acid dissolved in water, there is formed a violet coloured product, which, after extraction with chloroform, may be obtained in brilliant spangles. It is soluble in alcohol and acetic and sulphuric acids, and has approximately the composition required by the formula



When the diphenylcarbazide solution is added to more concentrated solutions of chromic acid, the violet coloration first produced gives place to a reddish-brown colour, and a mixture of hydrogen and nitrogen is evolved. A voluminous brown precipitate eventually separates, which, when washed with alcohol, leaves a maroon-coloured product which is insoluble in the usual solvents and contains 17.8 to 18.3 per cent. of chromium. The portion of the crude brown precipitate soluble in alcohol forms garnet-coloured spangles and is soluble in acetic acid: it contains 1.52 per cent. of chromium.

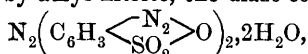
T. A. H.

Action of Bleaching Powder on Diazo- and *iso*Diazo-compounds. THEODOR ZINCKE and A. KUCHENBECKER (*Annalen*, 1903, 330, 1—37).—I. When bleaching powder is allowed to act on diazobenzenesulphonic acid, two substances are formed. 2 : 2'-Dinitro-azobenzene-4 : 4'-disulphonic acid, $\text{N}_2 \left[\text{C} \begin{smallmatrix} \text{C}(\text{NO}_2) \cdot \text{CH} \\ \text{CH} \end{smallmatrix} \right] \text{C} \cdot \text{SO}_3\text{H}]_2$, is obtained by adding a mixture of sodium sulphanilate and sodium

nitrite in aqueous solution to ice-cold sulphuric acid, and then pouring into the whole a solution of bleaching powder containing 4 per cent. of hypochlorous acid; the calcium salt slowly separates; the free acid prepared from the silver salt crystallises in slender, reddish-yellow needles; the *sodium*, *silver*, and *barium* salts (each with $2\text{H}_2\text{O}$) are described. 4:6-Dichloro-2-nitroaniline (m. p. 100°), which is also produced, is contained in the alcoholic washings of the calcium salt above mentioned.

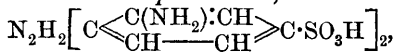
It is suggested that the initial product of the action of bleaching powder on diazobenzenesulphonic acid is a diazonium hypochlorite, which is then converted into a nitroamine; in the presence of acid, the latter changes into the isomeric nitrosulphanilic acid, which is oxidised by the bleaching powder to the azo-compound. The dichloronitroaniline is produced by chlorination of the nitrosulphanilic acid, when the sulphonic acid group is displaced by chlorine. By adding salt or concentrated calcium chloride to the solution containing the diazonium salt and the bleaching powder, a white solid separates, which is soluble in water and bleaches; it is possibly the impure diazonium hypochlorite.

2:2'-Diaminoazobenzene-4:4'-disulphonic acid, prepared by reducing the sodium salt of the dinitro-compound with 4 per cent. sodium amalgam, crystallises in pale brown needles with $2\text{H}_2\text{O}$; the alkali salts are very soluble in water, forming blood-red solutions; the *silver* salt crystallises in red, insoluble needles. The base can be diazotised in alcoholic solution by amyl nitrite, the diazo-compound,



being a yellow, insoluble powder, which does not dissolve in acids but in alkalis; it couples with β -naphthol. Azobenzene-4:4'-disulphonic acid is obtained as a by-product in the reduction of dinitroazobenzene-4:4'-disulphonic acid, and was isolated in the form of the sodium salt (Limpricht, Abstr., 1882, 1197).

On reducing the sodium salt of the dinitrosulphonic acid with zinc dust and water at 100° in the presence of ammonium chloride, *o*-diaminohydrazobenzene-4:4'-disulphonic acid,



is formed; its *sodium* salt is a colourless powder readily oxidising in the air. When the dinitroazo-compound is reduced by tin and hydrochloric acid, *o*-phenylenediamine-*p*-sulphonic acid is formed (Nietzki and Lerch, Abstr., 1889, 144).

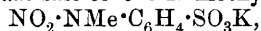
II. *Action of Bleaching Powder on Bromo-derivatives of Diazobenzene-3:3'-disulphonic Acid.*—When a solution of bleaching powder is added to a suspension of diazotised dibromo-*m*-sulphanilic acid in ice-cold water, a red solution is formed, and the calcium salt of *tetrabromazobenzene-3:3'-disulphonic acid*, $\text{N}_2\left[\text{C}\left\langle\begin{smallmatrix}\text{CH}\cdot\text{C}(\text{SO}_3\text{H})\\\text{CBr}\end{smallmatrix}\right\rangle\text{CH}\right]_2$, separates. The *sodium* salt, with $4\text{H}_2\text{O}$, forms a carmine-red, crystalline powder.

From *s*-tribromo-*m*-sulphanilic acid under a similar treatment, a very unstable substance is formed, which decomposes in alcoholic

solution, 3-chloro-2:4:6-tribromo-1-nitrobenzene being produced; it crystallises in yellow needles melting at 149—150°.

III. *Action of Bleaching Powder on Diazo-compounds not containing a Sulpho group.*—On adding a solution of bleaching powder to an ice-cold solution of benzenediazonium chloride, the liquid became milky, and a thick oil collected, which began immediately to decompose with the evolution of nitrogen; from the products of decomposition, 4:6-dichloro-2-nitroaniline was isolated by distilling with steam. From *p*-nitroaniline, a similar unstable oil was obtained, which yielded, with evolution of nitrogen, *p*-dinitroazobenzene (m. p. 216°).

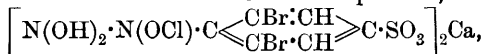
IV. *Action of Bleaching Powder on isodiazo compounds.*—On treating an aqueous solution of the sodium isodiazo oxide, derived from *p*-sulphanilic acid, with bleaching powder, the calcium salt of *p*-nitroaminobenzenesulphonic acid, $\text{NO}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$, separates; this substance was obtained and purified in the form of its normal sodium salt, $\text{NO}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{Na} \cdot \text{H}_2\text{O}$, which forms colourless crystals, decomposing in boiling water and converted by bleaching powder into the calcium salt of 2:2'-dinitroazobenzene-4:4'-disulphonic acid. The basic sodium, basic silver, basic barium, and normal barium salts are described. The potassium salt of the *N*-methyl ester,



is prepared by heating the basic potassium salt with methyl iodide in methyl alcoholic solution, and forms colourless crystals. Some of the salts just mentioned were obtained by Bamberger's method by oxidising the isodiazo oxide with permanganate. On reducing the nitroamine with sodium nitrite, the diazonium salt of benzene-*p*-sulphanilic acid was obtained; on reduction with tin and hydrochloric acid, *p*-sulphanilic acid was formed; with sodium amalgam, the hydrazine was produced.

The sodium salt of *p*-nitroisodiazo benzene was converted by bleaching powder into *p*-nitronitroaminobenzene (m. p. 110°). K. J. P. O.

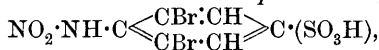
Action of Bleaching Powder on o-Dibromodiazobenzene-p-sulphonic Acid. WILHELM LENZ (*Annalen*, 1903, 330, 37—46. Compare preceding abstract).—In the action of bleaching powder on dibromobenzene-*p*-sulphonic acid, an intermediate product, a hypochlorite, can be isolated. 2:2':6:6'-Tetrabromoazobenzene-4:4'-sulphonic acid, $\text{N}_2 \left[\text{C} \begin{smallmatrix} \text{CBr} \cdot \text{CH} \\ \text{CBr} \cdot \text{CH} \end{smallmatrix} \right] \text{C} \cdot \text{SO}_3\text{H}$, is prepared by diazotising sodium dibromosulphanilate with sodium nitrite and sulphuric acid, and adding a solution of bleaching powder to the neutral suspension of the diazo-compound in water, when the calcium salt separates out. The sodium salt crystallises in dark red, lustrous needles with $2\text{H}_2\text{O}$. The calcium salt of the intermediate product,



is obtained by adding to a solution of the sodium dibromosulphanilate a solution of bleaching powder containing excess of calcium chloride; colourless needles separate, which soon become red and have an odour of hypochlorous acid; in aqueous solution, tetrabromobenzenazo-

4 : 4'-disulphonic acid is formed ; treatment with hydrochloric acid sets free chlorine. The *sodium* salt of this substance is prepared from *o*-dibromodiazobenzene-*p*-sulphonic acid by treatment with a solution of bleaching powder containing salt ; it is very soluble in water, and has all the characters of the calcium salt.

2 : 6-Dibromo-1-nitroaminobenzene-4-sulphonic acid,



is obtained by treating the calcium salt of the intermediate product with dilute hydrochloric acid ; the alcoholic solution of the solid product of the reaction deposits the normal calcium salt in soluble, colourless crystals. The basic *barium* (with $2\frac{1}{2}\text{H}_2\text{O}$), normal *sodium* (with H_2O), and basic *sodium* salts are described. On heating the calcium salt of the nitroamino-sulphonic acid with hydrochloric acid, the sulphonic acid group is displaced by the nitro-group, and 2 : 6-dibromo-4-nitroaniline (m. p. 204°) is formed. K. J. P. O.

Action of Bleaching Powder on Diazotised *m*-Xylidine-sulphonic Acid. ANTON MAUÉ (*Annalen*, 1903, 330, 46—49. Compare preceding abstracts).—On adding bleaching powder solution to the diazo-compound obtained from *m*-xylidinesulphonic acid, the calcium salt of *azo-m-xylene-5 : 5'-disulphonic acid* is obtained. The acid, $\text{N}_2 \left[\text{C} \begin{array}{c} \text{CMe} = \text{CH} \\ \text{CH} \cdot \text{C}(\text{SO}_3\text{H}) \end{array} \text{CMe} \right]_2 \cdot 5\text{H}_2\text{O}$, crystallises in reddish-yellow plates, which are very soluble in water (compare Jacobsen and Ledderboge, *Abstr.*, 1883, 593) ; the *silver* salt crystallises in reddish-yellow needles ; the *sodium* (with H_2O), basic *calcium* (with H_2O), normal *calcium* (with $3\text{H}_2\text{O}$), basic *barium* (with $\frac{1}{2}\text{H}_2\text{O}$), and normal *barium* (with $2\text{H}_2\text{O}$) salts are described. K. J. P. O.

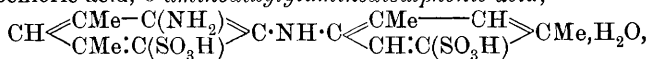
Action of Hydrogen Chloride and Hydrogen Bromide on Azobenzenedisulphonic Acids. THEODOR ZINCKE and A. KUCHENBECKER (*Annalen*, 1903, 330, 50—60. Compare preceding abstracts).—A study of the action of hydrogen chloride and bromide on various azobenzenedisulphonic acids has shown that chlorination or bromination takes place, the sulphonic acid group being replaced ; the azo-compound is often decomposed, and when methyl groups are present, as in xylene derivatives, diphenylamines are produced.

When the sodium salt of *o*-dinitroazobenzene-*p*-disulphonic acid is heated with concentrated hydrochloric acid under pressure at 160° for three hours, a small quantity of 3 : 4 : 3' : 4'-tetrachloroazobenzene, $\text{N}_2 \left(\text{C} \begin{array}{c} \text{CH} \cdot \text{CH} \\ \text{CCl} \cdot \text{CH} \end{array} \text{CCl} \right)_2$, is produced ; it crystallises in slender, flesh-coloured needles melting at 161 — 162° , and is reduced to 2 : 4-dichloroaniline. With hydrobromic acid, only a very small quantity of the tetrabromoazobenzene is formed ; it crystallises in red needles melting at 179° ; the main product of the reaction is 1 : 2 : 4 : 6-tetrabromobenzene (m. p. 98°).

4 : 6 : 4' : 6'-Tetrabromoazobenzene-3 : 3'-disulphonic acid is converted by hydrochloric acid into 2 : 4-dichloro-*m*-sulphanilic acid, which forms

small, colourless crystals; at the same time, a small quantity of 2:3:4-trichloroaniline (m. p. 68°) is produced. Under similar conditions, hydrobromic acid effects analogous decomposition, dibromo-*m*-sulphanilic acid being formed; but instead of a tribromoaniline, 2:3:4:6-tetrabromoaniline (m. p. 115°) is produced.

On heating the sodium salt of *m*-azo-xylenesulphonic acid with hydrochloric acid, *o*-aminodixylylaminedisulphonic acid,



is formed, and crystallises in yellow needles, which yield colourless alkaline solutions. K. J. P. O.

[Azo-compounds from Acyl-*p*-aminophenols.] DAHL & Co. (D.R.-P. 147530. Compare this vol., i, 207).—Azo-compounds are obtained by combining diazonium compounds with substituted acyl-*p*-aminophenols, in which an *ortho*-position to the hydroxyl is unoccupied. *Acetyl-4-aminophenol-2-sulphonic acid*, prepared by the action of acetic anhydride on an aqueous suspension of 4-aminophenol-2-sulphonic acid, forms white, soluble needles and melts and decomposes at a high temperature. *Acetyl-4-amino-2-chlorophenol*, prepared by boiling 2-chloro-4-aminophenol with glacial acetic acid, forms sparingly soluble, white needles and melts at 144°. *Acetyl-5-amino-2-cresol* forms white needles and melts at 179°. C. H. D.

Azo-compounds from Naphthylaminesulphonic Acids. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 148881 and 148882. Compare this vol., i, 207).—Azo-dyes may be prepared by diazotising 1-chloro- β -naphthylamine-5-sulphonic acid or β -naphthylamine-1:5-disulphonic acid and combining with resorcinol, 2:7-dihydroxynaphthalene, or 8-amino- α -naphthol-4-sulphonic acid. The products are very soluble in water or alkalis, but may be precipitated by acids.

1-Chloro- β -naphthylamine-5- or -7-sulphonic acids, or β -naphthylamine-1:6- or -1:7-disulphonic acids may also be diazotised and combined with β -naphthol. Red diazo-compounds having the formula $\text{OH} \cdot \text{C}_{10}\text{H}_5(\text{SO}_3\text{Na})\text{N} \cdot \text{N} \cdot \text{SO}_3\text{Na}$ appear to be formed in the case of naphthylaminedisulphonic acid, owing to the action of the sodium sulphite, resulting from the elimination of one sulpho-group, on the hydroxy-diazo-compound. C. H. D.

Disazo-compounds from 2:6-Diaminophenol-4-sulphonic Acid. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 148212).—2:6-Diaminophenol-4-sulphonic acid may be prepared by reducing 2:6-dinitrophenol-4-sulphonic acid with zinc dust and hydrochloric acid, adding sodium acetate, and precipitating with sodium chloride. It crystallises in white spangles, which become dark in air. Disazo-compounds of the type $\text{R} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{N}_2 \cdot \text{R}'$ may be prepared by adding one component to the acetic acid solution of the deep yellow tetraazo-compound, and, when the formation of the monoazo-derivative is complete, introducing the solution of the second component in alkali carbonate or hydroxide. C. H. D.

Isomerism of the Diazoxides. ARTHUR HANTZSCH (*Ber.*, 1904, 37, 1084—1087).—The conclusion of Zawidzki (*Abstr.*, 1903, i, 801), that an amphoteric electrolyte which has exceedingly feeble acid properties may nevertheless yield neutral salts with bases has been welcomed by Bamberger (*this vol.*, i, 201) as affording a possible explanation of the isomerism of the diazoxides, and has enabled him to suggest that the diazonium salts and the normal diazoxides may be regarded as derived from a common parent substance (the diazonium hydroxide), if the latter be regarded as an amphoteric electrolyte. As, however, Zawidzki's conclusions are not only in contradiction with the generally-accepted laws of electrochemistry, but have been shown to be based on incomplete evidence (*this vol.*, i, 381), this view can no longer be justified. T. M. L.

Azo-compounds containing a ψ -Aziminobenzene Residue. KALLE & Co. (D.R.-P. 148011).—Disazo-compounds prepared from diazotised *o*-nitroaniline or its derivatives and sulphonic acids of 8-amino-*a*-naphthol are reduced by sodium sulphide at low temperatures, forming azo-dyes which contain the ψ -aziminobenzene group. The reduction proceeds further on warming, the nitrogen ring being broken and *o*-diamines being produced. C. H. D.

Distribution of Nitrogen in the Proteid Molecule. THEODOR GÜMBEL (*Beitr. chem. Physiol. Path.*, 1904, 5, 297—312. Compare Hausmann, *Abstr.*, 1899, i, 653; 1900, i, 317; Kutscher, 1901, i, 107; Osborne and Harris, 1903, i, 585).—Osborne and Harris's conclusion that Hausmann's method is convenient and yields approximate results is supported by a number of experimental results. For the estimation of amide-nitrogen, distillation under reduced pressure at 40° is recommended (Schwarzchild, *Beitr. chem. Physiol. Path.*, 1903, 4, 155). The solubility of arginine phosphotungstate is less in the presence of an excess of phosphotungstic acid, and even when a solution (1 in 700) of 0.1 gram of arginine is precipitated and washed, the maximum loss is only some 10 per cent. Lysine behaves similarly to arginine, but histidine is appreciably soluble in a large excess of phosphotungstic acid. The precipitated phosphotungstates are at first flocculent and afterwards crystalline, and in the latter condition appear to be less soluble than in the former. The errors introduced by the precipitation of the phosphotungstates of monamino-acids and of melanine with the diaminophosphotungstates are small.

The distribution of nitrogen in serum albumin (15.93 per cent. of nitrogen) is amide, 1.01; melanine, 0.16; diamino, 5.30; monoamino, 9.61. The values for edestin agree with those of Hausmann and of Osborne and Harris. For keratin, amide, 1.17; melanine, 0.42; diamino, 2.95; monoamino, 11.81. For cartilage, amide, 1.35; melanine, 0.36; diamino, 1.35; monoamino, 7.95. For potassium chondrotinsulphate, amide, 35.27; melanine, 9.54; diamino, 32.78; and monoamino, 21.57 per cent. J. J. S.

Decomposition Products of Proteids containing Sulphur. KALLE & Co. (D.R.-P. 146947).—When proteid solutions or suspensions are heated with alkali sulphides, only traces of ammonia are pro-

duced, and compounds containing a larger quantity of sulphur than the original proteids are obtained. The product generally contains two compounds, one of which is precipitated from a solution of the sodium salt by acids, whilst the other is not. The alkali sulphide is best removed by dialysis. The product from egg albumin contains 15—15.5 per cent. of nitrogen and 2—2.5 per cent. of sulphur, that from casein contains 3—5.5 per cent. of sulphur. These compounds have the property of precipitating the heavy metals in a colloidal form from solutions of their salts.

C. H. D.

Action of Sulphur on Proteids. ARTHUR HEFFTER and MAX HAUSMANN (*Beitr. chem. Physiol. Path.*, 1904, 5, 213—233. Compare Rösing, *Abstr.*, 1892, 741).—The action of clear white of egg on sulphur has been studied. In many cases, 2 per cent. of sodium fluoride was added; this did not destroy the reducing action, and preserved the albumin. Other preservatives, such as toluene and chloroform, do not affect the evolution of hydrogen sulphide, nor does hydrocyanic acid. The temperature has but little influence, the addition of acid until the reaction with Congo-red is given tends to lessen the evolution of hydrogen sulphide, but the activity may be again restored by the addition of alkali. Saturation with sodium, potassium, or ammonium chloride, ammonium nitrate, or magnesium sulphate does not completely inhibit the evolution of hydrogen sulphide, whereas precipitation by saturation with ammonium sulphate or phosphate does. The evolution of gas is facilitated by the addition of a small amount ($\frac{1}{5}$ vol.) of alcohol, as this assists the solution of the sulphur, but is completely stopped by a large excess (2 vols.) of alcohol. The precipitate obtained by the addition of a large volume of alcohol reduces sulphur on the addition of water, whereas the clear filtrate from the precipitated albumin does not. Similarly, albumin precipitated by other reagents (acetic acid, phenol, or potassium ferrocyanide) has not lost its power of reducing sulphur. A few reagents, such as ferric chloride and copper sulphate, can completely destroy the property. Hydrolysis with pepsin hydrochloric acid has a similar effect.

The constituent of white of egg, which has the property of reducing sulphur, appears to be crystallised ovalbumin. White of egg also reduces arsenates to arsenites, nitrates to nitrites, iodates to iodides.

Selenium, phosphorus, sulphites and acid sulphites, methylene-blue, and indigotinsulphonic acid are not reduced; thiosulphates liberate hydrogen sulphide.

Cow's milk, as a rule, reduces sulphur to hydrogen sulphide; the reaction in many cases only begins after one or two days, and may be prevented by the addition of antiseptics. The evolution of sulphide in this case is attributed to the agency of micro-organisms.

Blood also reduces sulphur, and the active substance appears to be a compound soluble in water which is contained in the blood corpuscles.

Rösing's results with various organs (brain, liver, pancreas, &c.) are confirmed. The evolution of gas with calf's liver does not vary appreciably during the first 4—6 hours. When kept for 7 days, the

amount of hydrogen sulphide is found to be much smaller. Boiling decreases the amount of sulphide evolved.

The globulins of white of egg and of blood serum, fibrin, serum albumin, the proteids of milk, and other secretions have no reducing action on sulphur.

The hydrogen sulphide obtained by boiling proteids with sulphur and water may have an entirely different origin, since sulphur and boiling water and proteids and boiling water evolve hydrogen sulphide.

The oxidation is regarded not as a fermentation process nor as analogous to autoxidation, but as a mere removal of hydrogen atoms from the molecule of the substance oxidised. This view is confirmed by the fact that numerous carbon compounds, namely, benzyl mercaptan, thiophenol, thioglycollic acid, and sodium thioglycollate are readily oxidised by sulphur, evolving hydrogen sulphide. J. J. S.

Animal Glutins. III. Reactions with Salt Solutions. WL S. SADIKOFF (*Zeit. physiol. Chem.*, 1904, 41, 15—19. Compare this vol., i, 125, 126; Pauli, *Abstr.*, 1900, i, 265; 1902, ii, 388).—The solubilities of commercially pure gelatin, sinew trypsin-glutin A, nasal glutenin, tracheal glutenin, and aural glutenin in the following solutions have been investigated: potassium chloride, nitrite, and cyanide, sodium chloride, potassium bromide, iodide, thiocyanate, nitrate, and chlorate, ammonium nitrate and chloride, magnesium chloride, zinc chloride. The solutions employed were 50 per cent. solutions or cold saturated solutions. The different glutins are soluble in all the solvents with the exception of the four first named. Of these four, only sodium chloride dissolves commercial gelatin, none dissolve sinew trypsin-glutin A. The three glutenins are soluble in all the reagents.

Potassium nitrite and chloride solutions dissolve part of commercial gelatins, but the remainder is insoluble.

Heating the dry glutins decreases their solubility in salt solutions.

J. J. S.

Oxidation of Gelatin by Permanganate. GOSWIN ZICKGRAF (*Zeit. physiol. Chem.*, 1904, 41, 259—272. Compare *Abstr.*, 1903, i, 666; Lossen, *Annalen*, 201, 369; Pommerrenig, *Abstr.*, 1902, ii, 274).—It has been found that in the partial oxidation of gelatin by calcium permanganate the amount of guanidine increases as the biuret reaction diminishes. The conclusion is drawn that the biuret reaction of gelatin is due to the presence of an arginine residue in the molecule. J. J. S.

Protagon, Choline, and Neurine. WILHELM CRAMER (*J. Physiol.*, 1904, 31, 30—37).—The objections urged by Wörner and Thierfelder and by Lessem and Gies against the chemical individuality of protagon are not conclusive. Analyses give constant results when the material is prepared in various ways; a new method of preparation is given in the present paper. Protagon is not decomposed by warm ether or boiling alcohol. By decomposition with baryta water, choline is the only base formed. Choline can be readily

distinguished from neurine by their chromates, choline chromate being easily soluble, and neurine chromate almost insoluble in cold water.

W. D. H.

Pepsin-glutinopeptone. W. SCHEERMESSE (Zeit. physiol. Chem., 1904, 41, 68—98. Compare Siegfried, Abstr., 1903, i, 782).—Peptones are not immediately produced during the peptic digestion of gelatin; they appear to be formed indirectly from albumoses and make their appearance during the third day. A new peptone, *pepsin-glutino-peptone*, has been isolated by the iron alum method from the products of digestion of gelatin. Its molecular formula is $C_{23}H_{39}O_{10}N_7$, and it has $[\alpha]_D - 77$ — 78° approximately. It gives the biuret reaction readily, but not Molisch's reaction, and yields no precipitate with mercuric chloride, lead acetate, silver nitrate, potassium ferrocyanide, acetic acid, or metaphosphoric acid. Precipitates are obtained with tannic acid and in concentrated solutions with phosphotungstic acid. Barium and zinc salts have been prepared. On hydrolysis with 33.3 per cent. sulphuric acid, the peptone yields arginine, lysine, glutamic acid, and glycine.

The distribution of the nitrogen is as follows: amido-nitrogen, 0. Basic nitrogen, 25; of this 15.6 is due to arginine and 9.4 to lysine. Monoamino-nitrogen, 70 per cent., of which 10—11 is due to glutamic acid.

J. J. S.

Monoamino-acids from Salmin. EMIL ABDERHALDEN (Zeit. physiol. Chem., 1904, 41, 55—58. Compare Kossel, this vol., i, 211).—The following monoamino-acids have been isolated from the hydrolytic products from salmin by Fischer's esterification method: alanine, leucine, pyrrolidine-2-carboxylic acid, and probably phenylalanine and aspartic acid.

J. J. S.

Colouring Matter of Blood. I. J. HETPER and LEON MARCHLEWSKI (Zeit. physiol. Chem., 1904, 41, 38—41).—Mörner's β -hæmin is not a pure compound, its composition varies considerably with the physical conditions under which it is prepared, and it appears to be a mixture of acethæmin with several of its ether derivatives.

J. J. S.

Relationship of Chlorophyll and Hæmoglobin. LEON MARCHLEWSKI (Pflüger's Archiv, 1904, 102, 111—115. Compare Abstr., 1902, i, 387; 1903, ii, 677).—Largely polemical. A discussion of the results previously obtained by the author and others. The close relationship of the two pigments is regarded as certain, and the author maintains his priority in proving it.

W. D. H.

Lability and Activity of Enzymes. OSCAR LOEW (Pflüger's Archiv, 1904, 102, 95—110).—A theoretical discussion of the meaning of the term lability, and the mode of action of enzymes. Lability is increased by the amino-groups present.

W. D. H.

The Enzyme Melibiase, and Comparative Studies of Maltase, Invertase, and Zymase. ARMINIUS BAU (*Chem. Centr.*, 1904, i, 734; from *Zeit. Spiritusindustrie*, 27, 2—3, 9—10, 19—21, 29—31).—The effect of chemical reagents on melibiase and other yeast enzymes has been determined. Melibiase is contained in bottom fermenting yeast, and by its action melibiose is converted into dextrose and *d*-galactose. Contrary to Lindner's conjecture (*Woch. Brau.*, 17, 747) melibiase was found to resist the action of chemicals better than maltase, whilst invertase was the least affected and zymase the most. The activity of melibiase is not destroyed by drying, and, in one case, had not disappeared after remaining more than $5\frac{3}{4}$ years in the dry state; in this condition it may also be heated for a long time at 110° . Maltase prepared from either bottom or top fermenting yeast may also be dried (Bokorny, Abstr., 1901, i, 437); the activity of invertase is still less impaired by drying, whilst zymase is considerably more affected. The temperatures above which the zymases cease to be active were determined by experiments on yeast; for maltase, melibiase, and invertase these temperatures were found to be 55° , 70° , and 75° respectively. At 50° , the action of melibiase is at a maximum. Of the oxydases, lipases, and proteolytic enzymes also contained in the yeast cell, only the last have any action on the enzymes mentioned above. Invertase offers the greatest resistance to the action of proteolytic enzymes, maltase less than melibiase, and zymase the least of all. Melibiase occurs also in all the bottom fermenting yeasts of the Froberg and Saaz type, but is not present in top fermenting, wine, and wild yeasts. Other sources of melibiase are also mentioned in the original paper. E. W. W.

Preparation of Phenylsilicon Compounds. WALTHER DILTHEY and F. EDUARDOFF (*Ber.*, 1904, 37, 1139—1142. Compare Kipping, Proc., 1904, 19, 15).—When an ethereal solution of silicon tetrachloride (1 mol.) and magnesium phenyl bromide (8 mols.) is heated for three days on the water-bath, the principal product is triphenylsilicol, $\text{SiPh}_3\cdot\text{OH}$, which crystallises in fern-like groups of prisms and melts at 155° (compare Polis, Abstr., 1886, 618, and Kipping and Lloyd, Trans., 1901, 79, 449). When the compounds are only allowed to react at the ordinary temperature for a few hours, the principal product is *diphenylsilicol*, $\text{SiPh}_2(\text{OH})_2$, which crystallises from benzene in silky needles, melts at 138 — 139° , and dissolves readily in ether or chloroform, sparingly in light petroleum, and is insoluble in water. It loses 1 mol. of water on fusion and yields a gelatinous mass, which appears to be Kipping and Lloyd's diphenylsilicoketone, CPh_2O . C. H. D.

Organic Chemistry.

Action of Water on Trimethylene Dibromide and of Sulphuric Acid on Trimethylene Glycol. MARCELLUS RIX (*Monatsh.*, 1904, 25, 267—276. Compare Lieben, *Abstr.*, 1902, i, 336).—When heated in a sealed tube at 170° with 12 volumes of water, trimethylene dibromide yields propaldehyde, acetone, and trimethylene glycol. If less water is used, part of the propaldehyde condenses to methylethylacraldehyde. With 6 volumes of water at 150° for 30 hours, trimethylene dibromide yields phorone and mesitylic oxide, in addition to the above products.

Acetone, propaldehyde, and methylethylacraldehyde are obtained when trimethylene glycol is heated with dilute sulphuric acid at 170°. The glycol remains unchanged when heated with water at 215—220° for 2 days. G. Y.

Purifying and Characterising Alcohols. LOUIS BOUVEAULT (*Compt. rend.*, 1904, 138, 984—985).—The methods hitherto employed for purifying and characterising alcohols are unsatisfactory, owing to the fact that the alcohols are generally liquids, and yield liquid (esters) or readily soluble solid derivatives (phenylurethanes). The method described in this paper is free from these disadvantages, but is limited in application to those alcohols which form esters with pyruvic acid, and consists in converting the pyruvates into the semicarbazones, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CMe}\cdot\text{CO}_2\text{R}$, which are insoluble in water, slightly so in light petroleum, and fairly soluble in the other organic solvents, from which they crystallise easily; on treatment with alcoholic potassium hydroxide, the corresponding alcohol is regenerated. The following derivatives of primary or secondary alcohols were prepared: *ββ*-dimethylpropyl pyruvate semicarbazone, melting at 168°; *octyl* pyruvate semicarbazone, melting at 118—119°; *benzyl* pyruvate semicarbazone, melting at 176°; *phenylpropyl* pyruvate semicarbazone, melting at 143°; *hexahydrobenzyl* pyruvate semicarbazone, melting at 182°; and *βζ*-dimethyloctyl pyruvate semicarbazone, melting at 124°. The tertiary alcohols are decomposed on boiling with pyruvic acid, forming water and an ethylene hydrocarbon, the reaction affording a convenient method of preparing the latter. M. A. W.

Transformation of Amides into the Corresponding Primary Alcohols. ICILIO GUARESCHI (*Atti R. Accad. Sci. Torino*, 1904, 39, 418—420).—A claim for priority (compare Bouveault and Blanc, this vol., i, 213). W. A. D.

Hydrates of Methyl Alcohol and of Acetone. EUGÈNE VARENNE and L. GODEFROY (*Compt. rend.*, 1904, 138, 990—992).—The authors have measured the viscosity of aqueous solutions of methyl alcohol and of acetone by means of their constant pressure capillary viscosimeter [chronostiloscope] (compare this vol., i, 2;

ii, 160); the curves obtained by plotting these values as ordinates against the percentage composition of the mixture as abscissæ, indicate the existence of hydrates at singular points. Methyl alcohol forms six hydrates, the two most important being $\text{CH}_4\text{O}, 3\text{H}_2\text{O}$ and $\text{CH}_4\text{O}, \text{H}_2\text{O}$; the others are $\text{CH}_4\text{O}, 2\text{H}_2\text{O}$; $\text{CH}_4\text{O}, 5\text{H}_2\text{O}$; $\text{CH}_4\text{O}, 8\text{H}_2\text{O}$, and $\text{CH}_4\text{O}, 20\text{H}_2\text{O}$. Acetone forms three distinct hydrates with $3\text{H}_2\text{O}$, $4\text{H}_2\text{O}$, and $8\text{H}_2\text{O}$ respectively, and probably one having $34\text{H}_2\text{O}$.
M. A. W.

Composition of the Fusel Oil obtained in the Distillation of Acorns. TH. RUDAKOFF and A. ALEXANDROFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 207—219).—The fusel oil obtained in distilling acorns is qualitatively similar to that yielded by potato spirit, from which, however, it differs in quantitative composition. It contains about 2.7 per cent. of normal propyl alcohol, 9.8 of *isobutyl* alcohol, 87.4 of amyl alcohol containing about one-fourth of its weight of the active modification, together with very little normal hexyl alcohol, acetaldehyde, compound esters, and furfuraldehyde.
T. H. P.

Formation of Alcohols by Reduction of Acid Amides. RUDOLF SCHEUBLE and EMMO LOEBL (*Monatsh.*, 1904, 25, 341—353. Compare this vol., i, 3).—Reduction with sodium and amyl alcohol of palmitamide and stearamide leads to the formation of hexadecyl alcohol and octodecyl alcohol respectively. Suberamide is reduced by sodium and amyl alcohol to octomethylene glycol and octomethylenediamine. Lauramide is reduced in the same manner to dodecyl alcohol and dodecylamine, and a substance which melts at 195° . Lauramide is also reduced, but not so completely, by sodium and ethyl alcohol.
G. Y.

Action of Sulphuric Acid on Butan- α -diol. VIKTOR KADIERA (*Monatsh.*, 1904, 25, 332—340. Compare Lieben, Abstr., 1902, i, 336).— α -Dihydroxybutane (butan- α -diol) is not changed when heated with water at 200° for 8 hours. When heated with twice its volume of 10 per cent. sulphuric acid at 190° for 8 hours, α -dihydroxybutane yields ethylene, *n*-butaldehyde, methyl ethyl ketone, and α -ethyl- β -propylacraldehyde (Raupenstrauch, Abstr., 1887, 794).

When α -dihydroxybutane is allowed to remain in contact with 50 per cent. sulphuric acid, cooled by ice, butaldehyde and methyl ethyl ketone, but no ethylpropylacraldehyde, are formed.
G. Y.

Volatility of Carbon Compounds. LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1904, 42—63. Compare Abstr., 1903, ii, 8).—*Methyl isopropyl ether*, prepared by the interaction of methyl iodide with sodium isopropoxide, boils at 32.5° under 777 mm. pressure, has a sp. gr. 0.7347 at 20° and n_D 1.35756 at 20° . *Methyl tert.-butyl ether*, prepared similarly or by Reboul's method (Abstr., 1881, 1025), when methyl ψ -butyl ether and *isobutylene* are also formed, boils at 54 — 55° , has a sp. gr. 0.7578 and n_D 1.37566 at 20° . *isoPropyl tert.-butyl ether*, obtained by the action of *tert.*-butyl chloride on *isopropyl* alcohol or by heating a mixture of the two corresponding

alcohols with sulphuric acid, is a very mobile liquid, boils at $75-76^{\circ}$ under 768 mm. pressure, has a sp. gr. 0.7734 at 20° , and n_D 1.3858. Ethyl *tert.*-butyl ether boils at 70° under 758 mm. pressure, has sp. gr. 0.7519 at 20° and n_D 1.3794 at 20° (compare Reboul, *loc. cit.*, and Mamontoff, *J. Russ. Phys. Chem. Soc.*, 1897, 29, 230).

The boiling point in this series of ethers is dependent principally on the molecular weight; starting with methyl ether, the substitution of one hydrogen atom in one of the methyl groups by methyl leads to a rise in boiling point, but further similar substitutions produce, as the series is ascended, progressively smaller effects; the influence of the substituent group in elevating the boiling point decreases with the extent of alkylation, which has already been effected in the same group; thus, whereas the difference between the boiling points of ethyl and of propyl ethers is $33-34^{\circ}$, that between the boiling points of the respective isomerides methyl, propyl, and ethyl *tert.*-butyl ethers is 38° . The position in which substitution occurs appears to have but little effect on the boiling point. The boiling points of mixed ethers are not equivalent to the means of those of the two corresponding simple ethers, but are usually higher, and the difference is the more marked as the masses of the two alkyl radicles of the mixed ether are dissimilar. T. A. H.

Halogen Ether Oxides, $RO(CH_2)_nX$; their Magnesium Compounds, $RO \cdot [CH_2]_n \cdot MgX$; New Syntheses in the Tetramethylene Series. JULES HAMONET (*Compt. rend.*, 1904, 138, 975-977).— δ -Bromo- α -amyloxybutane, $C_5H_{11} \cdot O \cdot [CH_2]_3 \cdot CH_2Br$, obtained by the action of two mols. of hydrogen bromide on 1 mol. of $\alpha\delta$ -diamyloxybutane (compare Abstr., 1901, i, 187) in the cold, is a colourless liquid with an agreeable fruity odour, boils at $114-115^{\circ}$ under 16 mm. pressure, does not crystallise when cooled in a mixture of solid carbon dioxide and ether, and has a sp. gr. 1.14 at 18° . δ -Iodo- α -amyloxybutane, $C_5H_{11} \cdot O \cdot [CH_2]_3 \cdot CH_2I$, prepared by the action of sodium iodide on the preceding compound in alcoholic solution, is a slightly coloured liquid boiling at $128-129^{\circ}$ under 16 mm. pressure and having a sp. gr. 1.523 at 18° . This method of preparing halogen alkyloxy-compounds of the type $RO(CH_2)_nX$ appears to be a general one, $\alpha\epsilon$ -diamyloxy-pentane, $(CH_2)_5(OC_5H_{11})_2$, yielding ϵ -bromo- α -amyloxy-pentane, $(C_5H_{11}O)(CH_2)_5Br$, and $\beta\epsilon$ -diamyloxyhexane giving a corresponding derivative.

These halogen alkyloxy-compounds react with magnesium to form compounds of the type $RO \cdot [CH_2]_n \cdot MgX$, of which the following were prepared: $OMe \cdot [CH_2]_3 \cdot MgI$ from γ -iodo- α -methoxypropane,

$C_5H_{11} \cdot O \cdot [CH_2]_3 \cdot MgI$
from γ -iodo- α -amyloxypropane, $C_5H_{11} \cdot O \cdot [CH_2]_4 \cdot MgBr$ from δ -bromo- α -amyloxybutane, and $C_5H_{11} \cdot O \cdot [CH_2]_5 \cdot MgBr$ from ϵ -bromo- α -amyloxy-pentane.

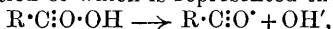
$\alpha\delta$ -Diamyloxybutane (compare Abstr., 1901, i, 187) is obtained by the action of amyloxybromomethane on the magnesium derivative of γ -iodo- α -amyloxypropane according to the equation:

$C_5H_{11}O \cdot [CH_2]_3 \cdot MgI + Br \cdot CH_2 \cdot OC_5H_{11} = MgBrI + (CH_2)_4(OC_5H_{11})_2$;
 $\alpha\delta$ -dimethoxybutane, $(CH_2)_4(OMe)_2$, prepared by a similar method, is a

very mobile liquid boiling at 132—133° under 760 mm. pressure, and has a sp. gr. 0.859 at 18°.

M. A. W.

Theory of Saponification. FRANZ GOLDSCHMIDT (*Zeit. Elektrochem.*, 1904, 10, 221—222).—Euler (*Abstr.*, 1901, ii, 307) concluded that the hydrolysis of esters points to their dissociation into negative alkoxyl ions and positive ions of the formula $R \cdot CO$. The author has independently reached the same conclusion by considering the saponification of fats. Sodium ethoxide reacts with a fat instantaneously, giving the ethyl ester of the fatty acid and the sodium salt of glycerol. Alcoholic potash gives the same result, the ethyl ester of the fatty acid subsequently undergoing saponification slowly. These changes are best explained by assuming that the fatty acid radicle behaves as a positive ion. These positive ions would be derived from a hypothetical base containing quadrivalent oxygen, the electrolytic dissociation of which is represented thus:



whereas the dissociation of the ordinary acid form is represented by the equation $R \cdot C \begin{smallmatrix} O \\ \diagup \\ OH \end{smallmatrix} \rightarrow (R \cdot C \begin{smallmatrix} O \\ \diagup \\ O \end{smallmatrix}) + H'$. From this point of view, acetyl chloride is regarded as the chloride of the basic ion $CH_3 \cdot CO'$, acetic anhydride as a compound of the ions $CH_3 \cdot CO'$ and $CH_3 \cdot CO \cdot O'$, or as acetyl acetate.

T. E.

Salts of Antimony with Organic Acids. III. EDUARD JORDIS (*Zeit. angew. Chem.*, 1904, 17, 330—334. Compare *Abstr.*, this vol., i, 216, 282).—Again a theoretical paper, a reply to Moritz and Schneider (*Abstr.*, 1902, i, 703).

A. McK.

Solubility of Some Salts of the Lower Fatty Acids. H. STANLEY (*Chem. News*, 1904, 89, 193).—The author has determined the solubility of barium and strontium formates and gives the results both in tabular form and in curves. Whilst the curve for calcium formate is practically a straight line (*Trans.*, 1902, 81, 355), those for these two salts are more pronounced. That for strontium formate, which crystallises with $2H_2O$, shows a break at a temperature of 83°, the solubility then decreasing as the temperature rises.

W. P. S.

Ferric Aceto-compounds. ARTHUR ROSENHEIM and PAUL MÜLLER (*Zeit. anorg. Chem.*, 1904, 39, 175—186).—Whilst normal ferric acetate, which is acted on by water to form the salt, $Fe(OH)_2 \cdot C_2H_3O_2$, is prepared by dissolving ferric hydroxide in aqueous acetic acid, the action is different when glacial acetic acid is used. When ferric hydroxide is boiled with glacial acetic acid for several hours, the undissolved product is *diferric penta-acetohydroxide*, $Fe_2(C_2H_3O_2)_5 \cdot OH$, which crystallises in dark red, microscopic plates. Its aqueous solution, which is bluish-red and odourless, is hydrolysed at the ordinary temperature, or more readily on warming, with formation of colloidal ferric hydroxide and acetic acid. The solution remains clear on being boiled, but the addition of an electrolyte, such as sodium chloride or sodium sulphate, causes the quantitative precipitation of

ferric hydroxide. The course of the hydrolysis in the cold was followed by determining the lowerings of the freezing point and the molecular conductivities of the solutions after definite periods. That a complex cation exists in solutions of diferric penta-acetohydroxide was indicated by the absence of a colour change in presence of potassium thiocyanate.

Ferric diacetochloride, $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_2\text{Cl}$, prepared from ferric chloride and glacial acetic acid, crystallises in reddish-brown needles. Concentrated aqueous solutions are dark red in colour and become yellow on dilution. Solutions which, to begin with, contain the complex cation, $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_2$ and the anion Cl , suffer hydrolytic dissociation with formation of ferric hydroxide and acetic acid when the solution is boiled; on cooling, the solution again contains the complex cation along with colloidal ferric hydroxide. This view was borne out by qualitative observations and by measurements of the lowering of the freezing point on the one hand, and by conductivity determinations on the other.

Ferric diacetobromide, $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_2\text{Br}$, prepared from ferric bromide and glacial acetic acid, forms dark brown needles and is more soluble in water than the chloride. In its solutions, the complex cation, $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_2$, is again present.

Tetraferric ennea-acetonitrate, $\text{Fe}_4(\text{C}_2\text{H}_3\text{O}_2)_9(\text{NO}_3)_3$, prepared by allowing a solution of ferric nitrate in boiling glacial acetic acid to crystallise, separates in ruby-red prisms. When more ferric nitrate is used, brown needles of *diferric penta-acetonitrate*, $\text{Fe}_2(\text{C}_2\text{H}_3\text{O}_2)_5\text{NO}_3 \cdot \text{H}_2\text{O}$, separate. It is probable that when those nitrates are dissolved in water, the ion is present in the complex cation.

Ferric diformyl chloride, $\text{Fe}(\text{HCO}_2)_2\text{Cl} \cdot 1\frac{1}{2}\text{H}_2\text{O}$, prepared from ferric chloride and anhydrous formic acid, forms a bright yellow, crystalline powder. A. McK.

Action of Chlorine on Anhydrous Acetates. ALBERT COLSON (*Bull. Soc. chim.*, 1904, 31, 422—430).—A résumé of work already published (Abstr., 1903, i, 396, 456, 601; and this vol., i, 3 and 134). T. A. H.

Decomposition of Some Trichloro- and Tribromo-acetates in Acetone. L. D. KOBOZEFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 247—255).—The author's investigations on the products obtained by the decomposition of potassium hydrogen trichloro- and tribromo-acetates in acetone solutions show that the first change taking place is according to the equation: $\text{CX}_3 \cdot \text{CO}_2\text{H} \cdot \text{CX}_3 \cdot \text{CO}_2\text{K} = \text{CX}_3\text{H} + \text{CO}_2 + \text{CX}_3 \cdot \text{CO}_2\text{K}$, where X represents chlorine or bromine. When all the free acid of the acid salt has been decomposed in this way, the water present in the acetone acts on the normal salt remaining, according to one of the following equations: (1) When the water is in excess, $\text{CX}_3 \cdot \text{CO}_2\text{K} + \text{H}_2\text{O} = \text{CX}_3\text{H} + \text{KHCO}_3$; (2) when insufficient water is present, $2\text{CX}_3 \cdot \text{CO}_2\text{K} + \text{H}_2\text{O} = 2\text{CX}_3\text{H} + \text{K}_2\text{CO}_3$. Finally, the chloroform or bromoform, under the influence of potassium carbonate, reacts with the acetone yielding trichloro- or tribromo-trimethylcarbinol.

T. H. P.

Decomposition of Trichloroacetic Acid and Some of its Salts in Aqueous Solution. WLADIMIR F. TIMOFÉEFF and L. D. KOBOZEFF (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 255—275).—In the decomposition of trichloroacetic acid in aqueous solution into chloroform and carbon dioxide, the constant of the velocity of the reaction, which is of the first order, diminishes very considerably with increase of concentration of the acid and becomes almost zero for very concentrated solutions. From this it is seen that the reaction proceeds at the expense of the active molecules of acid. The addition to the solution of trichloroacetic acid of an equivalent quantity of hydrochloric acid causes a large decrease in the constant; thus, at 87°, K falls from 0.0054 to 0.0036 (with hydrochloric acid). In the case of salts of trichloroacetic acid, which undergo a similar decomposition in aqueous solution, the water present must take part in the reaction in order to supply the hydrogen required for the formation of chloroform, and it is hence probable that water acts also in the decomposition of the acid. With potassium and sodium trichloroacetates, the velocity constant of decomposition falls rapidly as the reaction proceeds; that this is due to the accumulation of a salt of carbonic acid was shown by carrying out an experiment in presence of potassium carbonate, in which case K was found to be considerably less than before, but much more constant. To eliminate the influence of dissolved products of the reaction, the decomposition of barium trichloroacetate was studied, K in this case being found to be quite constant.

The decomposition of tribromoacetic acid in aqueous solution is also a reaction of the first order, and the constant is here much greater than with the chloro-acid at the same temperature.

According to the electrolytic dissociation theory, these decompositions would be expressed by the scheme: $\text{CCl}_3\cdot\text{COO}^- + \text{H}^+(\text{K, Na, ba}) + \text{H}_2\text{O} = \text{CHCl}_3 + \dots$, which would be an equation of the second (and, for the barium salt, perhaps the third) order; so that, like certain others, this reaction is not explained by the above theory.

It is, however, possible that the reaction may take place in the three phases: (1) preliminary hydration of the $\text{CCl}_3\cdot\text{COO}^-$ ions to $\text{CCl}_3\cdot\text{CO}(\text{OH})_2^-$; (2) decomposition of the latter at high temperatures into $\text{CHCl}_3 + \text{CO}_2 + \text{OH}^-$, and (3) combination of the OH^- and H^+ ions, and that only the second of these determines the velocity.

T. H. P.

Asymmetric Synthesis. WILLY MARCKWALD (*Ber.*, 1904, **37**, 1368—1370).—A reply to Cohen and Patterson (this vol., i, 366). A synthesis is "asymmetric" when, starting from a symmetrical compound, an asymmetrical product is obtained without the aid of any process of separation of isomerides. In the synthesis of active *l*-valeric acid from symmetrical methylethylmalonic acid (this vol., i, 221), the latter is converted quantitatively into the brucine salt, from which the active acid is obtained quantitatively. The presence of asymmetric ions is not essential, since the formation of the brucine salt takes place equally well in non-dissociating solvents.

C. H. D.

Combinations of Titanic Acid with Lactic Acid. CARL DREHER (D.R.-P. 149577).—Titanic acid dissolves only sparingly in lactic acid, but more readily in the presence of lactates of the alkalis or of the alkaline earths. A larger proportion of lactic acid and lactates is required to obtain a clear solution of titanic acid than in the corresponding case of the oxalates. The acid products obtained by evaporating the solutions are highly hygroscopic; alkalis convert them into neutral solutions or salts having a constitution approximating to the formula $\text{TiO}_2, \text{C}_3\text{H}_6\text{O}_3, 3\text{MC}_3\text{H}_5\text{O}_3$ or $\text{TiO}_2, 4\text{MC}_3\text{H}_5\text{O}_3$, according to the proportion of alkali employed. C. H. D.

Active Lactic and Malic Esters. EUGÈNE WASSMER and PHILIPPE A. GUYE (*J. Chim. Phys.*, 1903, i, 257—288).—The density, refraction, and dispersion, and the specific and molecular rotation and rotatory dispersion were determined for a number of esters. The first series consisted of the following derivatives of ethyl malate: ethyl propionyl-, butyryl-, hexoyl-, heptoyl-, octoyl-, pelargonyl-, and decoyl-malates. In this series, the specific rotation diminishes throughout from the propionyl- to the decoyl-compound, but the molecular rotation passes a maximum at the butyryl compound, after which it tends to a final limiting value. This was the case for all temperatures, and for light of various wave-lengths. The specific rotatory dispersion decreases as the series is ascended, but the molecular dispersion, whilst varying but slightly, passes through a maximum. The method of preparation of the active lactates is described. The second series of compounds consisted of the *l*- and *d*-propyl lactates, *d*-butyl lactate, *l*-isobutyl lactate, *l*-heptyl lactate, and *l*-octyl lactate. Owing to slight impurity in the ammonium zinc lactate from which the esters were obtained, the values for the rotation were multiplied by a correction factor. The specific rotation has a maximum for the octyl ester, the molecular rotation has no maximum and tends to a limiting value. The rotatory dispersion is almost equal for all the compounds, and is almost independent of temperature. The third series consisted of the acetyl-, propionyl-, butyryl-, and benzoyl derivatives of *l*-isobutyl lactate. In these, the specific rotation steadily decreases, the molecular rotation passes a maximum for the propionyl compound, whilst as in other series the dispersion is almost the same for the three allied compounds.

L. M. J.

Lactone of Hydroxycrotonic Acid and the γ -Substituted Crotonic Acids. ROBERT LESPIEAU (*Compt. rend.*, 1904, 138, 1050—1051).— $\beta\gamma$ -Dibromobutyramide, $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, prepared by dissolving the corresponding nitrile in fuming hydrobromic acid, melts at 86° , and when treated with dilute aqueous potassium hydroxide loses the elements of hydrogen bromide to form γ -bromocrotonamide, $\text{CH}_2\text{Br}\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{NH}_2$, which melts at 110° . γ -Bromocrotononitrile, $\text{CH}_2\text{Br}\cdot\text{CH}:\text{CH}\cdot\text{CN}$, prepared by heating $\beta\gamma$ -dibromobutyronitrile (compare Abstr., 1903, i, 547), is a viscid liquid boiling at 84° under 12 mm. pressure and melting at -14° ; when hydrolysed by hydrobromic acid, it yields $\beta\gamma$ -dibromobutyric acid, whilst with hydrochloric acid, it yields $\beta\gamma$ -dichlorobutyric acid, the

acid playing the triple rôle of saturating the ethylenic linking, hydrolysing the nitrile, and substituting chlorine for the bromine in the γ position. It is probable that in these reactions a lactone is first formed, which reacts with the halogen acid to give the substituted butyric acid, for if $\beta\gamma$ -dichlorobutyric acid is heated for 30 minutes at $200-215^\circ$ in a slow current of air, the lactone of *hydroxycrotonic acid*, $\text{CH}\cdot\text{CH}_2\text{CO}$, is produced; it is a viscid liquid boiling at $95-96^\circ$ under 13 mm. pressure and melting at $+4^\circ$, is soluble in water and precipitated by potassium carbonate, reduces ammoniacal silver nitrate with the formation of a mirror, slowly decolorises bromine, and gives with concentrated hydrobromic acid $\beta\gamma$ -dibromobutyric acid (compare Hill and Cornelison, Abstr., 1894, i, 319). M. A. W.

Ethyl Bromonitromalonate. RICHARD WILLSTÄTTER and VALENTIN HOTTENROTH (*Ber.*, 1904, 37, 1775—1787).—*Methyl bromonitromalonate*, $\text{NO}_2\cdot\text{CBr}(\text{CO}_2\text{Me})_2$, is a colourless neutral oil boiling at 133° under 16 mm. pressure; the *ethyl* ester boils at $136-137^\circ$ under 11 mm. pressure. *Methyl dihydroxymalonate* is deposited from benzene in colourless, columnar crystals, and from light petroleum in colourless needles melting at 77.5° ; the *ethyl* ester crystallises in large, transparent plates melting at 57° ; both compounds are obtained on heating the corresponding alkyl bromonitromalonates. The *dimethylamine* salt of methyl bromonitromalonate crystallises in faint yellow prisms melting at 150° , and is prepared by the action of dimethylamine in cold ethereal solution. *Bromodimethylamine*, NMe_2Br , is formed at the same time, but is better prepared (Berg's method for chlorodimethylamine, Abstr., 1895, ii, 297) by the interaction of sodium hypobromite and dimethylamine hydrobromide in cold aqueous solution. It is a yellow oil boiling at $64-66^\circ$.

Ethyl bromonitromalonate and ammonia interact in ethereal solution forming the ammonium salt of ethyl nitromalonate described by Franchimont and Klobbie (Abstr., 1889, 1143). By the interaction of methyl bromonitroacetate and concentrated aqueous ammonia, the ammonium salt of *bromonitroacetamide* is formed, the free amide crystallises from benzene or light petroleum in colourless needles or thin prisms melting at $80-81^\circ$. *Chloroiodoacetamide* was prepared by the action of ammonia on methyl chloroiodoacetate and subsequent fractional crystallisation; it forms colourless, glistening needles melting at $140-141^\circ$. E. F. A.

α -Methylparaconic Acid. FRITZ FICHTER and ERNST RUDIN (*Ber.*, 1904, 37, 1610—1614).—Ethyl pyrotartrate and ethyl formate condense in presence of sodium ethoxide, forming *ethyl β -hydroxymethylenepyrotartrate*, $\text{OH}\cdot\text{CH}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$, together with an isomeride, which may be *ethyl β -formylpyrotartrate*, $\text{CHO}\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$; they could not be completely separated.

Sodium amalgam reduces the hydroxymethylene compound only, forming *ethyl α -methylparaconate*, $\text{CO}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, which boils

at 145—150° under 14 mm. pressure. *α-Methylparaconic acid*, $C_6H_8O_4$, crystallises from absolute ether in large, transparent prisms, melts at 104°, and dissolves readily in water, alcohol, or chloroform, sparingly in ether or benzene. The *zinc* salt forms transparent, glistening prisms. On neutralising a hot solution of the acid with lime, hard crusts of *calcium α-methylitamalesate*, $C_6H_8O_5Ca$, separate. *α-Methylparaconic acid* decomposes partially on distillation, forming pyrocinchonic anhydride, but not vinylpropionic acid.

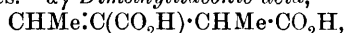
In the hydrolysis of ethyl *α-methylparaconate* with baryta, the barium salt of an acid, $C_8H_{12}O_5$, is obtained. The acid crystallises in short prisms, melts at 151°, and is probably *β-ethoxymethylenepyrotartaric acid*, $OEt \cdot CH : C(CO_2H) \cdot CHMe \cdot CO_2H$. C. H. D.

α-Methyl-Δ^β-pentenoic Acid. FRITZ FICHTER and ERNST RUDIN (*Ber.*, 1904, 37, 1615—1619).—Sodium amalgam reduces ethyl acetyrotartrate, $CH_3 \cdot CO \cdot CH(CO_2Et) \cdot CHMe \cdot CO_2Et$, to *αγ-dimethylparaconic acid*,

$$\begin{array}{c} O-CHMe \\ | \\ CO-CHMe \end{array} > CH \cdot CO_2H$$
, crystallising from water in slender needles or from ether in large, transparent prisms, melting at 131° and boiling at 195° under 14 mm. pressure. The *silver* salt forms slender needles. The *ethyl* ester forms a colourless liquid boiling at 142° under 14 mm. pressure, and has a sp. gr. 1.101 at 15°.

αγ-Dimethylparaconic acid decomposes when slowly distilled, yielding methylethylmaleic acid (Fittig and Parker, *Abstr.*, 1892, 814) and *α-methyl-Δ^β-pentenoic acid*, which are separated by crystallisation of their barium salts.

Methylethylmaleic anilide, $C_{12}H_{13}O_2N$, is a viscous liquid, boiling at 184° under 14 mm. pressure. Sodium hydroxide decomposes methylethylmaleic acid, forming methylethylfumaric and *αγ-dimethylitaconic acids*. *Methylethylfumaric acid*, $CO_2H \cdot CEt : CMe \cdot CO_2H$, forms small, granular crystals and melts at 202°. The *barium* and *calcium* salts form slender needles. *αγ-Dimethylitaconic acid*,



forms prismatic crystals and melts and decomposes at 148—150°.

α-Methyl-Δ^β-pentenoic acid, $CHMe : CH \cdot CHMe \cdot CO_2H$, forms a colourless liquid boiling at 198—199° under 740 mm. pressure, and has a sp. gr. 0.966 at 15° and $n_D = 1.44020$. The *calcium* salt forms slender needles. Boiling with sodium hydroxide converts the acid into methylethylacrylic acid (Lieben and Zeisel, *Abstr.*, 1883, 571).

C. H. D.

Action of Potassium Carbonate on *iso*Butaldehyde. FELIX M. A. KIRCHBAUM (*Monatsh.*, 1904, 25, 249—266. Compare Brauchbar, *Abstr.*, 1897, i, 137; 1898, i, 353).—Contrary to Brauchbar's statement, *diisobutaldehyde* is obtained along with octoglycol *isobutyrate*, and not alone, when *isobutaldehyde* is allowed to remain in contact with an equal volume of a saturated aqueous solution of potassium carbonate. The yield of *diisobutaldehyde* decreases with the use of anhydrous potassium carbonate or with an increase in the temperature of reaction. The best yield (86.66 per cent.) of octoglycol *isobutyrate* is obtained by the action of anhydrous

potassium carbonate at 65°, under which conditions no diisobutaldehyde is present after 60 hours. With 50 per cent. aqueous potassium carbonate, small amounts of products boiling below 100° under 17 mm. pressure, and, if the reaction is carried out at 125—130°, also products boiling above 138° under 17 mm. pressure are formed.

Octoglycol isobutyrate cannot be obtained free from diisobutaldehyde by fractional distillation under 17 mm. pressure, but must be distilled at 250° under atmospheric pressure, at which temperature diisobutaldehyde is decomposed. Diisobutaldehyde remains liquid after several months; Brauchbar's crystals melting at 90—92° could not be obtained. G. Y.

Methyl Ether of Acetylcarbinol, $\text{COMe} \cdot \text{CH}_2 \cdot \text{OMe}$. LOUIS HENRY (*Compt. rend.*, 1904, 138, 970—972).—The crystalline compound melting at 131° and boiling at 196°, which occurs as a secondary product in the preparation of acetylcarbinol (acetol) by the action of methyl alcohol on pyruvyl formate (compare Abstr., 1902, i, 736), and shown by Kling (compare following abstract) to be a polymeride of acetylcarbinyl methyl ether, has different physical and chemical properties (1) from the normal compound, which is a liquid boiling at 118°, having a sp. gr. 0.9570 at 20°, and reducing Fehling's solution (compare Abstr., 1881, 1121. Compare also Leonardi and de Franchis, Abstr., 1903, i, 787); (2) from the isomeric *methyl glycid*e, $\text{OMe} \cdot \text{CH}_2 \cdot \text{CH} \begin{smallmatrix} \text{CH}_2 \\ \diagup \\ \text{O} \end{smallmatrix}$, which boils at 118° and does not reduce Fehling's solution. M. A. W.

Methyl Acetolate. ANDRÉ KLING (*Compt. rend.*, 1904, 138, 972—975).—The polymeride of methyl acetolate (α -methoxy- β -keto-propane), obtained by Henry by the action of methyl alcohol on pyruvyl formate (compare Henry, Abstr., 1902, i, 736, and preceding abstract), also prepared by the direct action of methyl alcohol on acetylcarbinol at a temperature of 140°, is a crystalline compound which sublimes in long needles when heated and melts at 131°, is slightly soluble in water (1 part in 100) or methyl alcohol (4 parts in 100) or benzene, much more soluble in chloroform (20 parts in 100 at 15°). It does not reduce Fehling's solution, is not decomposed by boiling alkalis, does not react with phenylhydrazine acetate in the cold, but on warming forms the osazone of acetylcarbinol melting at 145°; is slowly attacked by boiling acid anhydrides to form methyl alcohol and the corresponding ethereal salt of acetylcarbinol; it is readily hydrolysed by dilute acids regenerating acetylcarbinol, slowly hydrolysed by water, and not attacked by the diastases (invertase, maltase emulsin, saline). The molecular weight, determined by the depression of the freezing point of benzene or ethylene bromide, shows that the substance is bimolecular, and the constitutional formula $\text{O} \begin{smallmatrix} \text{CMe(OMe)} \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CMe(OMe)} \cdot \text{CH}_2 \end{smallmatrix} \text{O}$ is suggested by the author. M. A. W.

Action of Hydrogen Peroxide on 1:2-Diketones and on α -Ketonic Acids. ARNOLD F. HOLLEMAN (*Proc. k. Akad. Wetensch. Amsterdam*, 1904, 6, 715).—Aqueous solutions of pyruvic acid,

benzoylformic acid, and thienylglyoxylic acid, when heated with the calculated amount of 30 per cent. hydrogen peroxide, were oxidised to acetic, benzoic, and thiophenic acids respectively.

Benzil, camphorquinone, and phenanthraquinone were also oxidised when dissolved in glacial acetic acid and then warmed for some days with a small excess of hydrogen peroxide, according to the general scheme, $R \cdot CO \cdot CO \cdot R' + HO_2H = R \cdot CO_2H + R' \cdot CO_2H$; camphorquinone first formed the anhydride, which was converted by boiling with dilute alkali into camphoric acid. A. McK.

Action of Calcium Hydroxide on *l*-Arabinose. HEINRICH KILIANI and F. KOEHLER (*Ber.*, 1904, 37, 1210—1215).—Details are given for preparing *l*-arabinose on the large scale from cherry-gum and for purifying the product. On agitating *l*-arabinose (1 part) during 14 days with water (10 parts) to which quicklime (0.2 part) had been added, and, after removing the lime with oxalic acid, extracting with ether, a considerable quantity of lactic acid was obtained, which was identified by means of its zinc salt; on dividing the insoluble residue into a number of fractions by dissolving in alcohol and precipitating with absolute ether, only syrups could be obtained which showed no tendency to crystallise and from which no definite hydrazide, hydrazone, or benzoate could be prepared. The original calcium salt was then fractionally precipitated with alcohol and the various fractions analysed; the numbers for the first two fractions agreed approximately with the formula $(C_5H_9O_5)_2Ca$; the later fractions having the composition $(C_6H_{11}O_6)_2Ca$. It thus appears that the acids formed contained carbon and oxygen in the ratio C:O = 1:1, as in the saccharic acids, and that from a C_5 sugar a C_6 acid had been synthesised. W. A. D.

Crystallised Melibiose. ARMINIUS BAU (*Zeit. Ver. deut. Zucker-Ind.*, 1904, 579, 481—521. Compare Abstr., 1902, i, 347).—Melibiose crystallises in the monoclinic system [$a:b:c = 1.92275:1:2.01243$; $\beta = 77^\circ 16'$]. The hydrated sugar has $[a]_D + 129.641^\circ$, the value for anhydrous melibiose being $+143.27^\circ$. It is hydrolysed by dilute hydrochloric, sulphuric, or oxalic acid, but not by lactic, citric, or tartaric acid; on long heating with the three last named organic acids, melibiose undergoes a diminution in its rotatory power, probably owing to the formation of esters of the acids. The actions of enzymes, at different temperatures, on melibiose were examined, and also the fermentation of the sugar by yeasts of various types. The copper reducing power was measured by boiling 50 c.c. of Fehling's solution in a porcelain beaker, adding 25 c.c. of the melibiose solution, and boiling for a further 4 minutes; if x is the amount of copper obtained, y_1 and y_2 the corresponding quantities of crystallised and anhydrous melibiose respectively, then:

$$y_1 = -0.0008 + 0.9731x + 0.310552x^2; \text{ and}$$

$$y_2 = -0.0007 + 0.88x + 0.2834x^2.$$

The means for detecting and estimating melibiose are described, and also its separation from other sugars and from starch conversion products. T. H. P.

Nitrocelluloses. II. CARL HAEUSSERMANN (*Ber.*, 1904, 37, 1624—1625. Compare this vol., i, 144).—The volatile product obtained on distilling nitrocellulose with alkali hydroxides may be distilled under reduced pressure, and is then obtained as a colourless, mobile oil, dissolving readily in water and boiling at 60—80° under atmospheric pressure. It readily yields iodoform, but does not reduce ammoniacal silver nitrate. Similar products are obtained from amorphous nitrocellulose, nitroamyloid, and the nitro-compounds of inulin, starch, lactose, and dextrose. C. H. D.

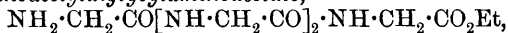
Purification of Leucine and Tyrosine by E. Fischer's Method of Esterisation. (*Trans. Guinness Res. Lab.*, 1903, 1, 57—60).—Leucine and tyrosine have been purified by the method proposed by Fischer (*Abstr.*, 1901, i, 192) for separating the monoamino-acids resulting from the hydrolysis of a proteid, consisting in esterifying the crude mixture of amino-acids by means of hydrochloric acid and alcohol, separating the free esters from their hydrochlorides by the action of concentrated alkali hydroxide solution at a low temperature, fractionally distilling the esters under 9—10 mm. pressure, and hydrolysing those fractions distilling below 85° by boiling for some hours with water in a reflux apparatus.

The leucine employed was a well-crystallised product prepared by Kahlbaum by the hydrolysis of the cervical ligament with acid, and gave the following results on examination: nitrogen (Kjeldahl's method), 10.3 (required 10.7) per cent.; nitrogen (Sachsse-Kormann method, nitrous acid), 6.8 (required 10.7) per cent.; $[\alpha]_D$ of 5 per cent. solution in 20 per cent. hydrochloric acid, +8.1° (required 17.6°). After purification of the leucine as above, it gave the following results: $[\alpha]_D$ +6.1°, this small number being probably due to partial racemisation; melting point on quickly heating, 280°; Cohn (*Abstr.*, 1895, ii, 25) observed 250° for an optically active leucine prepared by the pancreatic digestion of blood fibrin. Estimations of the nitrogen by the Sachsse-Kormann process gave 97.6, 101.1, and 100.0 per cent. of the theoretical amount; copper in the copper salt, 19.58 (required 19.64) per cent.

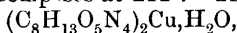
A sample of tyrosine obtained by the acid hydrolysis of horn-shavings gave, after purification: $[\alpha]_D$ in 17.5 per cent. hydrogen chloride solution, -8.17° (Fischer gave -8.6°); temperature of melting and decomposition, 287° (Lippmann gave about 235° and Fischer 310—314° for rapid heating); nitrogen by Kjeldahl's process, 7.65 (required 7.75) per cent. Another specimen of tyrosine, prepared by "chemolysis" of the albumin of ox-brain, was purified by dissolving in hydrochloric acid and precipitating by ammonia, after which it gave 7.70 per cent. of nitrogen by Kjeldahl's method; $[\alpha]_D$ in 20 per cent. hydrogen chloride solution, -2.92°; melting point, 360°; copper in copper salt, 14.50 (required 14.9) per cent. This specimen was found to be much less soluble in 20 per cent. hydrogen chloride solution than that prepared from horn-shavings, and is doubtless partially racemised. T. H. P.

The Spontaneous Decomposition of Glycine Ethyl Ester. THEODOR CURTIUS (*Ber.*, 1904, 37, 1284—1300).—Glycine ethyl ester decomposes spontaneously, forming glycine anhydride and the so-called "biuret base" (Curtius, *Abstr.*, 1883, 337). The latter was described by Schwarzschild (*Abstr.*, 1903, i, 780) as containing an open chain of seven glycine groups, but is now shown to contain only four such groups.

Ethyl aminoacetyldiglycylaminoacetate,

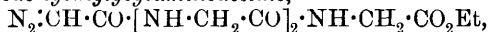


is best prepared by mixing pure ethyl glycine with absolute ether, air being excluded. The decomposition takes place very slowly, and pure biuret base is obtained. With impure ester, or in presence of moisture, the product contains considerable quantities of glycine anhydride, apparently in combination with the base. The ester crystallises from water in small tablets, sinters at 218° , and decomposes without melting at 270° . It is readily soluble in water, sparingly so in hot chloroform or ethyl acetate, almost insoluble in alcohol, ether, or benzene. Solutions of metallic salts give a large number of reactions characteristic of proteids. The *picrate* crystallises in long prisms and melts at 189° . The *hydrochloride* forms small tablets and melts and decomposes at 192 – 193° . The *platinichloride* forms bright orange tablets, containing $2\text{H}_2\text{O}$, and melts and decomposes at 112° . The *copper salt*,



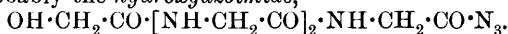
crystallises in bright blue tablets, becoming anhydrous and colourless at 110° and melting at 158 – 159° to a red liquid. The bright blue aqueous solution becomes red on addition of alkalis, and is decolorised by acids.

Ethyl diazoacetyldiglycylaminoacetate,

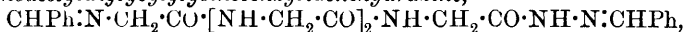


forms bright yellow tablets and becomes more intensely yellow at 130° , and melts and decomposes at 159° . Ammonia forms *diazoacetyldiglycylglycinamide*, crystallising in yellow tablets, blackening at 200° , and melting and decomposing at 240° . Iodine converts the diazo-ester into *ethyl di-iodoacetyldiglycylaminoacetate*, a white precipitate, sintering at 160° and melting and decomposing at 190° . Boiling the diazo-ester with water yields *ethyl hydroxyacetyldiglycylaminoacetate*, which forms slightly yellow crystals.

Hydrazine hydrate and the biuret base form *aminoacetyldiglycylglycinehydrazide*, $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO}[\text{NH} \cdot \text{CH}_2 \cdot \text{CO}]_2 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$, a white powder, not melted at 300° . The *hydrochloride* forms a colourless, highly hygroscopic mass, and decomposes at 112° . Sodium nitrite forms a colourless compound melting and decomposing at 79 – 80° , which is probably the *hydroxyazoimide*,



Benzaldehyde condenses with the hydrazide to form *benzylidene-aminoacetyldiglycylglycinebenzylidenehydrazine*,



melting at 228° .

Hippurazide condenses with the biuret base to form *ethyl benzoyl-tetraglycylaminoacetate*, $\text{COPh} \cdot [\text{NH} \cdot \text{CH}_2 \cdot \text{CO}]_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, which

darkens at 240° and melts and decomposes at 256—257°. The *hydrazide* melts at 272—274° and its *benzylidene* derivative at 275°.

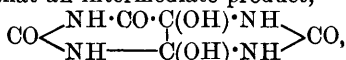
When the biuret base is heated for several hours at 100° in a vacuum, *octoglycine anhydride*, $(\text{NH}\cdot\text{CH}_2\cdot\text{CO})_8$, is obtained as an infusible substance which gives the biuret reaction. C. H. D.

Complex Compounds of Succinimide. LEO TSCHUGAEFF (*Ber.*, 1904, 37, 1479—1481).—When aqueous ammonia is cautiously added to a concentrated alcoholic solution of copper chloride and succinimide, a compound, $\left(\begin{array}{c} \text{CH}_2\cdot\text{CO} \\ | \quad \diagup \\ \text{CH}_2\cdot\text{CO} \end{array} \text{N} \right)_2\text{Cu}, 2\text{NH}_3$, is formed, crystallising in copper-red needles. With primary amines, similar compounds are formed; thus, the *allylamine* compound crystallises in long, silky, copper-red needles with a metallic lustre and the *benzylamine* derivative is similar. In aqueous solution, using a smaller quantity of ammonia, a compound of the type $\left(\begin{array}{c} \text{CH}_2\cdot\text{CO} \\ | \quad \diagup \\ \text{CH}_2\cdot\text{CO} \end{array} \text{N} \right)_2\text{Cu}, \text{NH}_3, 3\text{H}_2\text{O}$ is formed, crystallising in dark blue, prismatic needles; the *methylamine* derivative forms similar violet crystals. E. F. A.

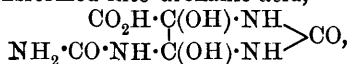
Preparation of Substituted Succinimides in Aqueous Solution. GUSTAV KOLLER (*Ber.*, 1904, 37, 1598—1599).—Substituted succinimides have hitherto been prepared by heating succinic acid with bases and distilling off the water formed. A more convenient method, yielding very pure products, is that of boiling succinic anhydride and primary amines suspended in water. The preparation of phenylsuccinimide, *p*-tolylsuccinimide, and β -naphthylsuccinimide is described. C. H. D.

Formation of Uroxanic Acid and of Allantoin from Uric Acid. ERNST E. SUNDBIK (*Zeit. physiol. Chem.*, 1904, 41, 343—347. Compare Claus, *Ber.*, 1874, 7, 227, and Abstr., 1895, i, 129).—A quantitative yield of allantoin may be obtained by oxidising uric acid with alkaline permanganate according to the method previously described for the preparation of uroxanic acid, except that the filtrate is immediately acidified with acetic acid.

It is suggested that an intermediate product,



is formed by the oxidation of uric acid, and that under the influence of alkali this is transformed into uroxanic acid,



but in the presence of acids into allantoin.

J. J. S.

Preparation of Alkali Cyanides. DEUTSCHE GOLD- & SILBERSCHNEIDE-ANSTALT VORM. ROESSLER (D.R.-P. 149678. Compare this vol., i, 380).—Not only solid carbon, but also a great variety of volatile organic compounds, react with fused sodamide to form disodium cyan-

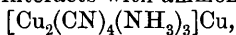
amide. Fused sodium or a lead-sodium alloy is heated at 400° and a current of mixed ammonia and acetylene in equivalent proportions is led in, the temperature being gradually raised to 550° . No sodium carbide is formed. When the whole is converted into disodium cyanamide, the temperature is raised to 750 – 800° , and carbon or acetylene added in sufficient quantity to form sodium cyanide. C. H. D.

Complex Cyano-copper-ammonia Compounds. FREDERICK P. TREADWELL and CONWAY VON GIRSEWALD (*Zeit. anorg. Chem.*, 1904, 39, 84–97).—Many of the complex cyano-copper-ammonia compounds described in the literature as uniform substances are not so. The compound $\text{Cu}_2(\text{CN})_3 \cdot 2\text{NH}_3$, best prepared by boiling cuprous cyanide with aqueous ammonia in the absence of air or by boiling the potassium cuprocyanides with water in the absence of air and then passing a current of ammonia until the cuprous cyanide, which separates at first, is redissolved, forms colourless crystals and is identical with the compound described by Malmberg. It is converted by boiling water into ammonia and cuprous cyanide. Its ammoniacal solution quickly assumes a deep blue tint on exposure to the atmosphere; blue needles separate after a time, and these in turn are converted into a green compound. When the potassium cuprocyanide of the composition $[\text{Cu}_2(\text{CN})_3, \text{H}_2\text{O}]\text{K}$ is treated with dry ammonia, it is converted into a compound of the probable composition $[\text{Cu}_2(\text{CN})_3, \text{NH}_3]\text{K}$, whilst the other potassium cuprocyanides, $[\text{Cu}_2(\text{CN})_4]\text{K}_2$ and $[\text{Cu}_2(\text{CN})_5]\text{K}_6$, are not acted on by ammonia.

Ammonium cuprocyanide, $[\text{Cu}_2(\text{CN})_3, \text{H}_2\text{O}]\text{NH}_4$, prepared from a mixture of freshly-precipitated cuprous cyanide and aqueous hydrocyanic acid by the action of ammonia, forms colourless, glassy, triclinic crystals. It parts with water at about 100° ; at about 120° , ammonium cyanide is produced, and finally metallic copper separates. When heated with ammonia in the absence of air, it forms the compound $[\text{Cu}_2(\text{CN})_2(\text{NH}_3)_2]$.

The compound $[\text{Cu}_2(\text{CN})_3(\text{NH}_3)]_2\text{Cu}$, prepared from the ammonium salt, $[\text{Cu}_2(\text{CN})_3, \text{NH}_3]\text{NH}_4$, by double decomposition with cupric acetate, forms a brown, amorphous powder.

The salt $[\text{Cu}_2(\text{CN})_3(\text{NH}_3)_2]_2\text{Cu}$, best prepared by boiling the compound $[\text{Cu}_2(\text{CN})_3, \text{H}_2\text{O}]\text{NH}_4$ with ammonia, crystallises in violet, rhombic leaflets; it is also formed by prolonged boiling of the compound $\text{Cu}_2(\text{CN})_4(\text{NH}_3)_4\text{Cu}$, which separates in blue needles when potassium cuprocyanide interacts with ammonia. The salt



prepared by passing hydrogen cyanide into an ammoniacal solution of cupric oxide, forms glistening, green, rhombic needles. When acted on by mineral acids, hydrogen cyanide and cupric cyanide are formed; at 120° , it evolves ammonia. When alcohol is added to its concentrated ammoniacal solution, the salt $[\text{Cu}_2(\text{CN})_4(\text{NH}_3)_4]\text{Cu}$ is precipitated; it forms long, blue needles, which readily part with ammonia to form the green salt. A. McK.

Electrolysis of Potassium Double Cyanides. H. VON HAYEK (*Zeit. anorg. Chem.*, 1904, 39, 240–256).—The electrolytic oxidation

of potassium ferrocyanide was examined with the view of ascertaining the experimental conditions under which complex oxidation occurs, and of finding the influence of concentration on the current yield and current density. The liquid at the anode should be kept in constant motion by a stirrer, and should be kept alkaline in order to prevent the formation of free hydroferrocyanic acid. The space occupied by the anode should be twice as great as that occupied by the cathode. The rotating anode should present as large a surface as possible. The electrodes were made of nickel. The potassium ferrocyanide and ferricyanide were estimated by the methods of de Haen and Gintl. A current yield of 100 per cent. can be attained. The concentration of the electrolyte exercises, within very wide limits, no influence on the yield. The limit to which the concentration of the total electrolyte may be lessened increases with increasing original concentration; the limit to which the concentration of the solution at the anode may be diminished is independent of the original concentration and of the amount of potassium ferricyanide formed. With regard to the influence of the current density on the current yield, it was found that if a definite limit of the current density were exceeded whilst the concentration was constant, secondary processes set in, and their intensity increased rapidly, whilst the current yield sank to a corresponding degree. The maximum value of the current density which may be employed increases with increase of concentration. The secondary processes mentioned are: (1) the decomposition of water by the anion $\text{Fe}(\text{CN})_6$, whereby free alkali at the anode will be neutralised, (2) the electrolytic decomposition of the potassium ferrocyanide formed, and (3) the electrolytic decomposition of the potassium hydroxide present.

When potassium manganicyanide, $\text{K}_3\text{Mn}(\text{CN})_6$, is electrolysed, the solution is first dissociated into the ions K_3 and $\text{Mn}(\text{CN})_6$. The final product of the cathodic reduction is manganous hydroxide. The stability of the anion $\text{Mn}(\text{CN})_6$ is distinctly less than that of the ion $\text{Fe}(\text{CN})_6$.

Potassium nickel cyanide, $\text{K}_2\text{Ni}(\text{CN})_4$, undergoes electrolytic dissociation into the ions K and $\text{Ni}(\text{CN})_4$. The final product of the cathodic reduction was a substance which was not isolated owing to its instability, but which, on exposure to the atmosphere, was rapidly converted into the original double cyanide. The stability of the anion $\text{Ni}(\text{CN})_4$ is slight; it splits up readily into $\text{Ni}(\text{CN})_2$ and $(\text{CN})_2$.

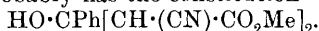
Potassium cobalticyanide, $\text{K}_3\text{Co}(\text{CN})_6$, undergoes electrolytic dissociation into the ions K_3 and $\text{Co}(\text{CN})_6$. The final product at the anode is the oxide, Co_2O_3 . The stability of the anion $\text{Co}(\text{CN})_6$ is slight. The oxidation at the anode was more marked in this case than with the other compounds examined, since oxides of nitrogen and ozone were produced.

A. McK.

Preparation of Platinocyanides. ANDRÉ BROCHET and JOSEPH PETIT (*Compt. rend.*, 1904, 138, 1095—1097).—See this vol., ii, 414.

Condensation Products of Cyanoacetic Esters with Acylcyanoacetic Esters. CH. SCHMITT (*Bull. Soc. chim.*, 1904, 31, 529—530. Compare Abstr., 1903, i, 398).—When an excess of

methyl cyanoacetate is employed in preparing methyl benzoylcyanacetate by Haller's process, and especially when the reaction product is heated on the water-bath after the whole of the alcohol has been driven off, there is formed a substance $C_{15}H_{14}O_5N_2$, which crystallises from alcohol, melts at 162° , is insoluble in water or ether, and is hydrolysed by potassium hydroxide dissolved in alcohol, into methyl cyanoacetate, methyl benzoylcyanacetate, and benzoic acid. It gives no coloration with ferric chloride, but is coloured yellow by alkalis, belongs to the series of compounds investigated by Guinchant (Abstr., 1896, i, 594), and probably has the constitution



From acetyl chloride and methyl cyanoacetate under the same conditions, the substance $C_{16}H_{19}O_5N_3$, is obtained; this is slightly soluble in alcohol, acetone, and chloroform, and insoluble in other solvents. When hydrolysed with potassium hydroxide dissolved in alcohol, there are formed methyl cyanoacetate, acetic acid, and an acid, $C_{13}H_{14}O_5N_2$, which melts at $158-160^\circ$.
T. A. H.

Diazo-fatty Esters. THEODOR CURTIUS and E. MÜLLER (*Ber.* 1904, 37, 1261—1279).—Very few diazo-fatty esters have hitherto been prepared in a pure state (compare Curtius and Koch, Abstr., 1889, 376). Only esters of α -amino-acids yield diazo-esters; β - and γ -amino-esters, on the other hand, do not form diazo-compounds, and an $\alpha\beta$ -diamino-ester therefore yields an α -diazo- β -hydroxy-ester. It is not possible to purify the diazo-esters by fractional distillation, but the method of distillation with steam from an excess of barium hydroxide may be employed with success (Abstr., 1884, 42). From a comparison of the fatty diazo-compounds, the rule is deduced that only fatty compounds in which the amino-group, carbonyl, and at least one hydrogen atom are attached to the same carbon atom yield diazo-compounds with nitrous acid.

Ethyl diazosuccinate, $CO_2Et \cdot C(N_2) \cdot CH_2 \cdot CO_2Et$, remains on evaporating its dry ethereal solution in a vacuum as a yellow oil, which has a sp. gr. 1.132 at $18^\circ/4^\circ$ and n_D 1.4615 at 18° , and decomposes violently at 120° under 10 mm. pressure (compare Curtius and Lang, Abstr., 1892, i, 451).

Ethyl phenylalanine hydrochloride, $CH_2Ph \cdot CH(NH_2) \cdot CO_2Et, HCl$, melts at 127° and reacts with sodium nitrite to form *ethyl phenylalanine nitrite*, $CH_2Ph \cdot CH(NH_2) \cdot CO_2Et, HNO_2$, an unstable, white, crystalline mass (compare ethyl glycine nitrite, Abstr., 1888, 576). In presence of dilute sulphuric acid, *ethyl α -diazo- β -phenylpropionate*, $CH_2Ph \cdot C(N_2) \cdot CO_2Et$, is formed, and is obtained after distillation from barium hydroxide as a golden-yellow oil with aromatic odour, becoming viscous in liquid air and boiling undecomposed at $90-94^\circ$ under 11 mm. pressure. It has a sp. gr. 1.107 at $20^\circ/4^\circ$ and n_D 1.5367 at 16° . Dilute mineral acids decompose it only on warming. The crude ester is partially converted on distillation into *ethyl α -hydroxy- β -phenylpropionate*, $CH_2Ph \cdot CH(OH) \cdot CO_2Et$, a colourless oil boiling at 126° under 15 mm. pressure.

Methyl phenylalanine, $CH_2Ph \cdot CH(NH_2) \cdot CO_2Me$, is a colourless liquid, which boils at 141° under 12 mm. pressure, and has a sp. gr. 1.096

at $22^{\circ}/4^{\circ}$ and n_D 1.5203 at 20° . The *hydrochloride* forms yellow needles and melts and decomposes at 158° . *Methyl α -diazob- β -phenylpropionate* boils at 85 — 87° under 12 mm. pressure and is less stable towards acids than the ethyl ester. It has a sp. gr. 1.126 at $20^{\circ}/4^{\circ}$ and n_D 1.5435 at 26° .

Ethyl α -diazopropionate, $N_2 \cdot CMe \cdot CO_2Et$, from ethyl alanine, is a yellow oil, readily decomposed by acids. It boils at 65 — 68° under 41 mm. pressure, solidifies to a crystalline mass in solid carbon dioxide and ether, and has a sp. gr. 1.086 at $12^{\circ}/4^{\circ}$ and n_D 1.4472 at 18° . The methyl ester is similar, and boils at 43 — 45° under 11 mm. pressure, and has a sp. gr. 1.101 at $13^{\circ}/4^{\circ}$ and n_D 1.4487 at 20° . Both esters partially decompose on distillation, forming esters of dimethylfumaric acid.

Ethyl α -aminobutyrate hydrochloride, $CH_2Et \cdot CH(NH_2) \cdot CO_2Et, HCl$, from α -aminobutyric acid, melts at 130.5° and forms ethyl α -diazobutyrate, $CH_2Et \cdot C(N_2) \cdot CO_2Et$, a yellow oil which boils at 63 — 65° under 11 mm. pressure and has a sp. gr. 1.028 at $21^{\circ}/4^{\circ}$ and n_D 1.4460 at 21° .

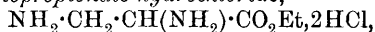
Methyl α -aminobutyrate hydrochloride melts at 139° . Methyl α -diazobutyrate is an orange-yellow oil, which boils at 54 — 56° under 12 mm. pressure and has a sp. gr. 1.043 at $18^{\circ}/4^{\circ}$ and n_D 1.4465 at 24° .

Ethyl α -diazohexoate, $CH_2Pr \cdot C(N_2) \cdot CO_2Et$, from ethyl leucine hydrochloride (E. Fischer, Abstr., 1901, i, 192), forms a yellow oil, which boils at 70 — 73° under 12 mm. pressure and crystallises in liquid air. It has a sp. gr. 0.9605 at $15^{\circ}/4^{\circ}$ and n_D 1.4329 at 19° . Iodine and ammonia convert it into *di-iodohexoamide*, $CH_2Pr \cdot Cl_2 \cdot CO \cdot NH_2$, which crystallises from water in small, bright yellow, sparingly soluble needles and darkens at 180° , decomposing and evolving iodine at higher temperatures.

Ethyl β -aminopropionate, from β -alanine, reacts with nitrous acid in the presence of hydrochloric acid to form ethyl β -hydroxypropionate, together with a small quantity of ethyl β -chloropropionate. In similar manner, ethyl β - and γ -aminobutyrate yield ethyl β - and γ -hydroxybutyrate respectively.

Ethyl β -amino- α -hydroxypropionate yields ethyl $\alpha\beta$ -dihydroxypropionate. Ethyl hexahydroanthranilate (Einhorn and Meyenberg, Abstr., 1894, i, 591) yields ethyl hexahydrosalicylate.

Ethyl $\alpha\beta$ -diaminopropionate hydrochloride,



from hippurylaspartic acid, melts and decomposes at 142 — 144° and reacts with sodium nitrite to form ethyl α -diazob- β -hydroxypropionate, $OH \cdot CH_2 \cdot C(N_2) \cdot CO_2Et$, a yellow oil.

Diazo-compounds could not be obtained from the ethyl esters of tyrosine or phenylglycine.

C. H. D.

Cacodylic Acid and Amphoteric Substances. PAUL THIEBAUT MULLER and ED. BAUER (*Compt. rend.*, 1904, 138, 1099—1100).—Zawidzki's conclusion that cacodylic acid is a pseudo-acid (compare Abstr., 1903, i, 801; this vol., i, 232) is not supported by the physico-chemical properties of the acid (compare Hantzsch, this vol., i, 381), also the molecular refraction for the D ray of $N/4$ cacodylic acid at 20° is 23.95, whilst that of its sodium salt under the same conditions is 25.53; the difference, 1.58, between these two values is

characteristic of weak carboxylic acids and points to the acid and the salt having the same constitution (compare Abstr., 1903, i, 77, 78; ii, 705); further, the heat of neutralisation of cacodylic acid is 14.11 Cal. (compare Imbert, Abstr., 1900, i, 145), and hence its heat of dissociation is +0.4 Cal., equal to that of acetic acid but of opposite sign, and the temperature coefficient of the affinity constant K of cacodylic acid is therefore not abnormal. M. A. W.

Synthesis of Benzene Hydrocarbons by Reduction of Oxygenated Groups. AUGUST KLAGES and CH. STAMM (*Ber.*, 1904, 37, 1715—1721).—*iso*Durenesulphonic acid, prepared from *isodurene* by the action of fuming sulphuric acid, crystallises in glistening leaflets, melts at 79—80°, and is decomposed with formation of *isodurene* when heated at 100° with phosphoric acid. Dibromo-*isodurene* melts at 199°; when heated at 180—200° with hydriodic acid, it is converted into mesitylene, which is also formed when *isodurene* is heated with hydriodic acid and red phosphorus at 180—200°. Ethylmesitylene is obtained by reduction of vinylmesitylene with sodium and alcohol, or of ethyl mesitylcarbinol with hydriodic acid. The sulphonic acid is decomposed by phosphoric acid at 100°. Dibromoethylmesitylene melts at 59—60°, not at 219° (Thöl and Tripke, *Ber.*, 1895, 28, 2462), and yields mesitylene when heated with hydriodic acid at 200°.

Propylmesitylene is obtained by the reduction of mesitylethylcarbinol with hydriodic acid and red phosphorus. The sulphonic acid is decomposed by phosphoric acid at 100°. Propylmesitylene yields mesitylene when heated with hydriodic acid at 250—260°. *iso*Butylmesitylene, $C_6H_2Me_3 \cdot CH_2P_1\beta$, is prepared by reducing mesitylisopropyl carbinol; it is a colourless oil, which boils at 125—127° under 24 mm., at 228—230° under 745 mm. pressure, has a sp. gr. 0.8782 at 18°/4°, and n_D 1.5004 at 13°. It remains unchanged when heated with hydriodic acid at 200°. The sulphonic acid is decomposed by phosphoric acid at 100°.

*iso*Pentylmesitylene boils at 133—135° under 19 mm., at 241—243° under 747 mm. pressure, has a sp. gr. 0.8751 at 23°/4°, n_D 1.4976 at 23°, and is only slightly decomposed by hydriodic acid at 200°. The sulphonic acid is an oil, soluble in water. With bromine in aqueous solution, it yields dibromoisopentylmesitylene, which crystallises in colourless needles and melts at 44°.

Heptylmesitylene is a colourless oil, which boils at 157—158° under 15 mm., at 271—272° under 750 mm. pressure, has a sp. gr. 0.8753 at 17°/4° and n_D 1.4970 at 17°, and is not acted upon by hydriodic acid at 250°. The sulphonic acid yields a magnesium salt $C_{32}H_{50}O_6S_2Mg$, which crystallises in small leaflets. G. Y.

Derivatives of *m*-Di-iodobenzene with Polyvalent Iodine. CONRAD WILLGERODT and A. DESAGA (*Ber.*, 1904, 37, 1301—1310. Compare Abstr., 1903, i, 743, 745, 746).—A solution of *m*-di-iodobenzene in chloroform absorbs chlorine, forming *m*-iodophenyl iododichloride, $C_6H_4I \cdot ICl_2$, which crystallises in slender, yellow needles, decomposes at 112°, and dissolves in organic solvents. The further action of chlorine produces yellow, silvery leaflets of *m*-phenylene

di-iodotetrachloride, $C_6H_4(ICI_2)_2$, decomposing at 122° and dissolving readily in benzene or acetone, sparingly in ether, chloroform, or acetic acid.

m-Iodoiodosobenzene, $C_6H_4I \cdot IO$, forms a bright yellow, amorphous powder, insoluble in organic solvents, and explodes on heating at temperatures varying with the rapidity of heating. Dry hydrogen chloride or phosphorus pentachloride converts it into the chloride. Glacial acetic acid forms transparent needles of *m-iodophenyl iododiacetate*, $C_6H_4I \cdot I(OAc)_2$, melting at 160° . The *basic sulphate*, $[C_6H_4I \cdot I(OH)]_2SO_4$, decomposes at 108° . The *basic nitrate* was only obtained in an impure state. The *basic chromate* is a red, amorphous precipitate.

m-Di-iodosobenzene, $C_6H_4(IO)_2$, forms a bright yellow, amorphous powder, insoluble in all solvents, and explodes at 108° . Acetic acid forms *m-phenylene di-iodotetraacetate*, $C_6H_4[I(OAc)_2]_2$, a snow-white powder melting at 204° . The reddish-yellow *chromate* is unstable and explodes at 60° .

m-Iodoiodoxybenzene, $C_6H_4I \cdot IO_2$, crystallises from boiling water in colourless needles and explodes violently at $216-218^\circ$. *m-Di-iodoxybenzene*, $C_6H_4(IO_2)_2$, forms white, microscopic tablets and explodes violently at 261° , and also on percussion.

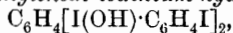
Phenyl-m-iodophenyliodinium hydroxide, $C_6H_4I \cdot IPh \cdot OH$, from *m-iodoiodosobenzene* and iodoxybenzene with silver oxide, is obtained as a strongly alkaline solution in water. The *chloride* crystallises in white, readily soluble needles and melts at 134° , the sparingly soluble *bromide* forms small leaflets and melts at 169° , the insoluble yellow *iodide* decomposes at 89° . The *periodide*, $C_6H_4I \cdot IPh \cdot I_3$, forms small, reddish-brown needles and melts at 118° . The *dichromate* forms an orange precipitate and decomposes at 135° , the colourless, amorphous *mercurichloride* melts at 56° , and the amorphous, flesh-coloured *platinichloride* melts at 187° .

Di-m-iodophenyliodinium hydroxide, $I(C_6H_4I)_2 \cdot OH$, has only been obtained in solution. The *chloride* crystallises from benzene in small needles and melts at 156° , the *bromide* forms an amorphous powder and decomposes at 163° , the yellow *iodide* melts at 141° , the reddish-yellow *dichromate* darkens at 85° , and the *platinichloride* darkens at 109° and melts at 191° .

Iodophenyldi-m-iodophenyliodinium hydroxide, $C_6H_4I \cdot I(C_6H_3I_2) \cdot OH$, from *m-iodoiodosobenzene*, is obtained in solution. The *bromide* forms a yellow, amorphous precipitate and melts at 109° , the *iodide* forms a chestnut-brown precipitate and blackens at 52° , the *dichromate* is red and decomposes at 91° , the *platinichloride* is flesh-coloured, and sinters at 120° and melts at 171° .

Dichloroethyl-m-iodophenyliodinium chloride, $C_2H_3Cl_2 \cdot ICl \cdot C_6H_4I$, prepared from *m-iodophenyl iodochloride* and silver acetylde-silver chloride, crystallises from water in white needles and melts at 148° .

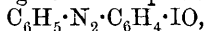
Di-m-iodophenyl-m-phenylenedi-iodinium hydroxide,



is obtained in the form of a strongly alkaline solution. The *bromide* sinters at 58° and melts at 146° , the pale yellow, unstable *iodide* decomposes at 140° , the *platinichloride* melts at 176° , and the red *dichromate* at 146° .

C. H. D.

Derivatives of *p*-Iodoazobenzene and *m*-Chloriodobenzene with Polyvalent Iodine. CONRAD WILLGERODT and GEORGE MCPHAIL SMITH (*Ber.*, 1904, **37**, 1311—1317. Compare Abstr., 1903, i, 743, 745, 746; preceding abstract).—*p*-Iodoazobenzene (Noelting and Werner, Abstr., 1891, 211) absorbs chlorine in solutions in chloroform and acetic acid, forming *azobenzene-p-iodochloride*, $C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot ICl_2$, which separates in large, red, monoclinic tablets and decomposes slowly when heated, finally melting at 100° . *p*-Iodosoazobenzene,



forms a yellowish-red powder, insoluble in most solvents, and melts and decomposes at 105° . The *acetate*, $C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot I(OAc)_2$, forms rosettes of ruby-red crystals and melts and decomposes at 164° . *p*-Iodoxyazobenzene, $C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot IO_2$, forms a red, amorphous, insoluble powder and explodes at 189° .

p-Benzeneazophenyliodinium hydroxide, $C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot IPh \cdot OH$, is only obtained in solution. The *chloride* forms rosettes of dark red needles and melts at 205° ; the *bromide* forms yellowish-red crystals and melts at 164° ; the *iodide* forms long, bright yellow, silky needles and melts at 135° , the *dichromate* and *platinichloride* crystallise from hot water and decompose on heating; the *mercurichloride* crystallises in short, red needles and decomposes at 152 — 156° . Yellow ammonium sulphide at low temperatures forms a *polysulphide*, closely resembling antimony sulphide, and decomposing above 0° to a heavy oil.

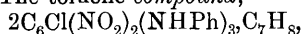
Di-m-chlorophenyliodinium hydroxide, $(C_6H_4Cl)_2I \cdot OH$, is obtained in solution from *m*-chloriodoso- and *m*-chloriodoxy-benzene (Willgerodt, Abstr., 1893, i, 699). The *chloride* crystallises from water in slender needles and melts at 175 — 177° ; the *bromide* forms colourless needles and melts at 155° ; the *iodide* separates from alcohol in colourless needles and melts at 132° ; the *dichromate* forms large, orange needles and melts and decomposes at 143° ; the *platinichloride* forms golden, glistening leaflets, and the *mercurichloride* forms white needles and melts at 180 — 182° .

Phenyl-m-chlorophenyliodinium hydroxide, $C_6H_4Cl \cdot IPh \cdot OH$, is obtained in solution only. The *chloride* forms long, slightly grey needles and melts at 163° ; the *bromide* forms glistening, white needles and melts at 164° ; the *iodide* forms small, white needles and melts at 130° ; the *dichromate* melts and decomposes at 128° ; the *platinichloride* forms orange leaflets and melts and decomposes at 169° , and the *mercurichloride* forms colourless needles and melts at 122 — 126° .

C. H. D.

Tetrachlorodinitrobenzene. C. LORING JACKSON and H. A. CARLTON (*Amer. Chem. J.*, 1904, **31**, 360—386. Compare Abstr., 1903, i, 79—80).—When 1 : 2 : 3 : 5-tetrachloro-4 : 6-dinitrobenzene is heated with aniline for 3 hours at 100° , it is converted into 2-chloro-4 : 6-dinitro-1 : 3 : 5-triaminobenzene, $C_6Cl(NO_2)_2(NHPh)_3$, which has a dark red colour, melts at 179° , and is freely soluble in ether, chloroform, acetone, carbon disulphide, hot glacial acetic acid, or hot benzene. This substance has a strong tendency to form additive compounds, in which the added substance appears to be attached similarly to water of crystallisation in salts, and is expelled at 100° . On crystallisation

from benzene, the compound $C_6Cl(NO_2)_2(NHPh)_3, C_6H_6$ is obtained as dark crimson plates; the compound $2C_6Cl(NO_2)_2(NHPh)_3, C_6H_6$ forms orange-red needles. The toluene compound,

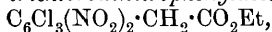


crystallises in brilliant, orange-coloured needles. The acetic acid compound, $C_6Cl(NO_2)_2(NHPh)_3, C_2H_4O_2$, forms long, orange-coloured needles. The chloroform compound, $C_6Cl(NO_2)_2(NHPh)_3, CHCl_3$, crystallises in dark red prisms and gradually loses chloroform at the ordinary temperature. An attempt was made to prepare the chloride of chlorodinitrotrianilinobenzene, but without success.

2-Chloro-1:3:5-tribromobenzene melts at $90-91^\circ$. On nitration, it yields 2-chloro-1:3:5-tribromo-4:6-dinitrobenzene, which crystallises in white prisms, melts at 208° , is freely soluble in ether, benzene, chloroform, acetone, carbon disulphide, or hot glacial acetic acid, and by the action of aniline is converted into chlorodinitrotrianilinobenzene, identical with that obtained from tetrachlorodinitrobenzene.

When a solution of tetrachlorodinitrobenzene in benzene is boiled for 10 minutes with sodium ethoxide, chlorodinitrophenylglucitol diethyl ether is produced together with tetrachlororesorcinol diethyl ether, $C_6Cl_4(OEt)_2$, which crystallises from alcohol in white, slender needles, melts at 73° , and is freely soluble in ether, benzene, chloroform, light petroleum, acetone, glacial acetic acid, or carbon disulphide.

By the action of ethyl sodiomalonate on tetrachlorodinitrobenzene, ethyl trichlorodinitrophenylmalonate, $C_6Cl_3(NO_2)_2 \cdot CH(CO_2Et)_2$, is obtained, which crystallises from alcohol in short, white prisms, melts at 82° , and dissolves readily in ether, benzene, chloroform, acetone, glacial acetic acid, or carbon disulphide. When the crude product of this reaction is distilled with steam, the residue contains a substance which is probably ethyl trichlorodinitrophenylacetate,



which crystallises from alcohol in long, slender, white needles, melts at $87-88^\circ$, and is easily soluble in ether, benzene, chloroform, acetone, glacial acetic acid, or carbon disulphide; the corresponding acid crystallises in white prisms, melts at $190-191^\circ$, and dissolves readily in alcohol, ether, chloroform, or acetone; its silver salt is of a pale yellow colour.

E. G.

Nitration of Fluorobenzene. ARNOLD F. HOLLEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 6, 659-665. Compare this vol., i, 232).—Whilst *p*-fluoronitrobenzene is quantitatively converted into *p*-nitroanisole by the action of sodium methoxide, *m*-fluoronitrobenzene is hardly acted on at all when treated with sodium methoxide under the same conditions. It is thus possible to determine quantitatively the amounts of *p*- and *m*-fluoronitrobenzene in a mixture containing the two. Similarly, 1-fluoro-2:4-dinitrobenzene can be separated from *p*-fluoronitrobenzene, and it is accordingly possible to estimate any fluoro-di- or -*m*-nitrobenzene present in the nitration product of fluorobenzene. *o*-Fluoronitrobenzene is readily converted into the dinitro-compound. The product, formed by

nitrating 10 grams of fluorobenzene at 0° with a mixture of 25 c.c. of nitric acid of sp. gr. 1.48 and 5 c.c. of nitric acid of sp. gr. 1.51, consists of 6.1 per cent. of *o*-fluoronitrobenzene, 4.1 per cent. of *m*-nitrobenzene fluoride, and 89.8 per cent. of *p*-fluoronitrobenzene; on further nitration of this product, a mixture containing 9 per cent. of fluorodinitrobenzene, 4 per cent. of the meta- and 87 per cent. of the para-compound.

The product obtained by nitrating fluorobenzene at -30° is similar to that obtained at 0° . A. McK.

Additive Compounds of *s*-Trinitrobenzene. PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 6, 702. Compare Hibbert and Sudborough, *Trans.*, 1903, 83, 1334).—*s*-Trinitrobenzene combines with anthracene to form orange-red needles melting at 161° , with methylantracene to form red needles melting at 138° , with phenanthracene to form an orange-yellow compound melting at 163° , and with fluorene to form a yellow compound; in those cases, 1 mol. of *s*-trinitrobenzene is combined with 1 mol. of the hydrocarbon.

s-Trinitrobenzene forms with α -bromonaphthalene a lemon-yellow compound melting at 139° , and a similar one with dibenzylideneacetone.

s-Trinitrobenzene also interacts with anthranilic acid, methylantranilate, *p*-aminoacetophenone, ethyl *m*-aminobenzoate, and ethyl *p*-aminobenzoate to form coloured crystalline compounds. A. McK.

Formation and Decomposition of Diphenylmethane Derivatives. KARL AUWERS (*Ber.*, 1904, 37, 1470—1479).—A theoretical discussion of the formation of diphenylmethane derivatives from the ψ -phenols. E. F. A.

Arylated Ethylenes and their Reduction to Arylparaffins. AUGUST KLAGES and SEBASTIAN HEILMANN (*Ber.*, 1904, 37, 1447—1457. Compare *Abstr.*, 1902, i, 668; Hell and Stockmayer, this vol., i, 241).—*as*-Diphenylethylene is oxidised by air with formation of formaldehyde, which, in a glass vessel, polymerises to trioxymethylene (Tiffeneau, *Abstr.*, 1903, i, 81).

$\alpha\beta$ -Diphenylpropane, obtained by reduction of $\alpha\beta$ -diphenylpropylene, boils at 285 — 286° (corr.) (see Silva, *Abstr.*, 1880, 259; Krämer, Spilker, and Eberhardt, *Abstr.*, 1891, 207).

Diphenylpropylcarbinol, $\text{CH}_2\text{Et}\cdot\text{CPh}_2\cdot\text{OH}$, formed by the action of benzophenone on magnesium propyl iodide, melts at 65° and boils at 162 — 163° under 11 mm. pressure. The *chloride*, $\text{CH}_2\text{Et}\cdot\text{CPh}_2\cdot\text{Cl}$, is a yellow oil, and when heated with pyridine at 125° yields *aa*-diphenylbutylene, $\text{CPh}_2\cdot\text{CHEt}$, which is a colourless oil, boils at 154° under 20 mm., at 286° (corr.) under 750 mm. pressure, and has a sp. gr. 1.030 at $18^{\circ}/4^{\circ}$. It decolorises potassium permanganate solution and forms an additive compound with bromine.

aa-Diphenylbutane, obtained by reduction of diphenylpropylcarbinol with zinc dust and a mixture of glacial acetic acid and hydriodic acid, or with hydriodic acid and red phosphorus, boils at 140 — 142°

under 11 mm., at 265—266° under 751 mm. pressure. *aa*-Diphenylbutylene is only slightly reduced by sodium and alcohol (compare Masson, Abstr., 1903, i, 21).

Phenylbenzylethylcarbinol, $\text{CH}_2\text{Ph}\cdot\text{CETPh}\cdot\text{OH}$, obtained from ethyl iodide and deoxybenzoin, is a colourless, viscid oil which boils at 179° under 14 mm. pressure. The *chloride*, formed by the action of thionyl chloride on the carbinol, yields $\alpha\beta$ -diphenylbutylene when heated with pyridine at 172°. $\alpha\beta$ -Diphenylbutylene, $\text{CHPh}\cdot\text{CETPh}$, distils in two fractions, at 164—167° and 168°. After some days, the two oils deposit thick, strongly refractive crystals which melt at 57°; the resulting liquid distils at 296—297°, yielding an oil which again slowly deposits crystals. The crystalline and liquid diphenylbutylenes are considered to be probably *cis*- and *trans*-isomerides (compare Sidborough, Abstr., 1892, 1224). Both isomerides yield additive compounds with bromine, and are oxidised by potassium permanganate and dilute sulphuric acid to benzoic acid and phenyl ethyl ketone.

$\alpha\beta$ -Diphenylbutane, obtained by reduction of $\alpha\beta$ -diphenylbutylene, is a colourless, odourless oil which boils at 152° under 11 mm., or at 288—289° under 751 mm. pressure.

Diphenylhexylcarbinol, $(\text{C}_6\text{H}_{13})\cdot\text{CPh}_2\cdot\text{OH}$, formed by the action of phenyl hexyl ketone on magnesium phenyl bromide, is a colourless oil which boils at 200—201° under 11 mm. pressure.

aa-Diphenylheptylene, $\text{CPh}_2\cdot\text{CH}\cdot\text{C}_5\text{H}_{11}$, formed from the carbinol through the chloride, is a colourless oil having a slight odour, has a sp. gr. 0.9673 at 18°/4°, and n_D 1.5648, and is only slightly soluble in alcohol. The action of bromine on diphenylheptylene in carbon disulphide solution leads to the formation of an oily *dibromide*, in glacial acetic acid solution to evolution of hydrogen bromide and formation of a *monobromo*-derivative, $\text{CPh}_2\cdot\text{CBr}\cdot\text{C}_5\text{H}_{11}$, which crystallises in delicate needles and melts at 74°.

aa-Diphenylheptane, obtained by reduction of the heptylene, is a colourless oil which boils at 180° under 10 mm., at 333—334° (corr.) under 751 mm. pressure, and is perhaps identical with Auger's diphenylheptane (Abstr., 1887, 814).

Diphenylbenzylcarbinol (Hell and Wiegandt, this vol., i, 490) is formed by the action of deoxybenzoin or of ethyl phenylacetate on magnesium phenyl bromide. The *chloride* is a colourless oil, which, when heated with pyridine, yields *triphenylethylene*; this melts at 62°, distils at 220—221° under 14 mm., or at 348—349° (corr.) under 751 mm. pressure, and yields a *dibromide* which melts at 92°. Triphenylethane, obtained by reduction of triphenylethylene, is identical with Biltz' triphenylethane formed from triphenylvinyl alcohol (Abstr., 1897, i, 533).

Phenyldibenzylcarbinol, $\text{CPh}(\text{CH}_2\text{Ph})_2\cdot\text{OH}$, formed by the action of ethyl benzoate on magnesium benzyl chloride, crystallises in small, colourless needles and melts at 86—87°.

Triphenylcarbinol, $\text{C}(\text{CH}_2\text{Ph})_3\cdot\text{OH}$, formed by the action of ethyl phenylacetate on magnesium benzyl chloride, crystallises in broad, glistening needles, melts at 114—115°, and boils at 383° (corr.) under 753 mm. pressure. It is probably identical with Houben's product, melting at 108—111° (Abstr., 1903, i, 826).

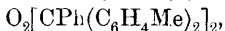
G. Y.

Specific Gravity and Thermal Expansion of Solutions of Naphthalene in Various Organic Solvents. CARL FORCH (*Festschr. Ludwig Boltzmann*, 1904, 696—705. Compare Abstr., 1903, ii, 632).—The solvents employed were chloroform, toluene, carbon disulphide, and ether. The value of the expression $(s - Q)/m$, where s and Q are the specific gravities of solution and solvent respectively and m is the molecular concentration of the naphthalene, increases with falling concentration in toluene, carbon disulphide, or ether; in chloroform solutions, the reverse is the case. In every case, the specific gravity observed is less than is to be expected from the specific gravities of the solvent and of solid naphthalene; that is, there is an increase of the molecular volumes. A noteworthy illustration of this is the fact that a 32 per cent. solution of naphthalene in carbon disulphide is lighter than solid naphthalene. J. C. P.

Triphenylmethyl. VIII. MOSES GOMBERG (*Ber.*, 1904, 37, 1626—1644. Compare Abstr., 1901, i, 77, 319, 638, 690; 1902, i, 534, 600, 754; 1903, i, 81, 244, 472; this vol., i, 32).—Substituted triphenylmethyl compounds have been obtained by the action of metals on substituted triphenylcarbinol chlorides. Most of these have not been isolated in the free form, but as peroxides.

Tri-*p*-tolylchloromethane, obtained by Friedel-Craft's synthesis or by Grignard's reaction, when treated in benzene solution with finely-divided (molecular) silver in the absence of air, yields an orange-yellow solution which contains a strongly unsaturated compound. When the solution is kept, the colour disappears, the unsaturated characteristics are no longer exhibited, and, on evaporation, a syrup corresponding in composition and molecular weight with *hexatolyethane* is obtained. If a current of air is passed through the benzene solution of the tritolychloromethane in the presence of silver, *tri-p-tolylmethyl peroxide*, $O_2[C(C_6H_4Me)_3]_2$, is obtained, the yield varying from 20—40 per cent. It crystallises from hot benzene or hot ether in large, glistening crystals melting at 169—170°. The same product is obtained when tritolychloromethane in benzene solution is oxidised with an aqueous sodium peroxide solution in the presence of a little acetic acid. Hydrolysis with a mixture of sulphuric and acetic acid yields the carbinol.

[With A. J. LYNN].—*Phenyldi-p-tolylchloromethane* melts at 106—107° and the corresponding carbinol at 79—80°. The *peroxide*,



is soluble in ether, but insoluble in light petroleum, and melts at 147—148°.

Diphenyl-*p*-tolylchloromethane, obtained from benzophenone chloride, toluene, and ferric chloride in the presence of carbon disulphide, may be converted into a *peroxide*, $O_2(CPh_2 \cdot C_6H_4Me)_2$, melting at 170—171°.

p-Chlorotriphenylchloromethane, $C_6H_4Cl \cdot CPh_2Cl$, obtained from benzophenone chloride, chlorobenzene, and aluminium chloride or from *p*-chlorobenzophenone chloride (Overton, Abstr., 1893, i, 208) and benzene with aluminium chloride, melts at 87° and gives a *peroxide* melting at 165° and insoluble in ether. *p*-Bromotriphenylchloromethane

melts at 111° and the *peroxide* obtained from it at 167° ; the corresponding *p*-*iodo*-compound melts at 119° and the *peroxide* at 169° .

[With L. H. CONE.]—*Tri-p-chlorotriphenylchloromethane*,
 $\text{CCl}(\text{C}_6\text{H}_4\text{Cl})_3$,

obtained from carbon tetrachloride, chlorobenzene, and aluminium chloride under certain conditions, melts at 146 – 148° and yields a *peroxide* (?) melting at 140 – 142° .

Diphenyl- α -naphthylchloromethane, obtained from benzophenone chloride, naphthalene, and aluminium chloride in presence of carbon disulphide, melts at 169° . It dissolves in concentrated sulphuric acid yielding a bluish-green solution and evolving hydrogen chloride. The *peroxide* is obtained as a crystalline precipitate insoluble in most organic solvents.

Tri-p-nitrophenylcarbinol chloride may be obtained by the action of phosphorus pentachloride on the corresponding carbinol at 170 – 180° . The carbinol melts at 189° (E. and O. Fischer, *Annalen*, 1878, 194, 255, gave 171 – 172°) and when pure dissolves in alkalis to a colourless solution. The *peroxide* obtained by the action of silver on solutions of the carbinol chloride in ethyl acetate and subsequent oxidation by atmospheric oxygen appears to be identical with the compound previously described (Abstr., 1901, i, 78), although it melts at 218° .

Comparative experiments in the rates of polymerisation of certain of these triphenyl methyl derivatives have been conducted by keeping the benzene solutions in sealed tubes for some time and noticing the loss of colour and of the unsaturated properties.

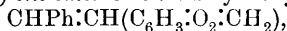
Although triphenylmethyl in solution has been shown to be bimolecular, this is attributed to association, and the simple formula CPh_3 is retained. J. J. S.

α -Phenylstilbene and the Methylene Ether of 3:4-Dihydroxystilbene. CARL HELL and FR. WIEGANDT (*Ber.*, 1904, 37, 1429–1432. Compare this vol., i, 242).—Benzophenone, either fused or in ethereal solution, is added to an ethereal solution of magnesium benzyl chloride, and, after treatment with dilute hydrochloric acid, the ether is distilled off. The fraction of the residue distilling at 200 – 240° under 12–15 mm. pressure contains diphenylbenzylcarbinol. If the residue is heated to 300° before distillation, the fraction distilling at 200 – 240° is α -phenylstilbene.

Diphenylbenzylcarbinol, $\text{CH}_2\text{Ph}\cdot\text{CPh}_2\cdot\text{OH}$, crystallises in long, glistening needles and melts at 88 – 89° .

α -Phenylstilbene, $\text{CHPh}\cdot\text{CPh}_2$, crystallises in small leaflets, melts at 67 – 68° , and forms an additive compound with bromine, which easily loses hydrogen bromide.

The action of piperonal on magnesium benzyl chloride leads to the formation of the *methylene ether* of 3:4 dihydroxystilbene,

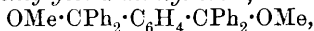


which distils at 225 – 250° under 12 mm. pressure, crystallises in glistening needles, and melts at 95 – 96° .

The *dibromide*, obtained by the action of bromine on the methylene ether in chloroform solution, forms small, white crystals and melts at 188° . G. Y.

A Quinonoid Hydrocarbon. JOHANNES THIELE and HANS BALHORN (*Ber.*, 1904, 37, 1463—1470).— ω -Hexabromo-*p*-xylene, $\text{CBr}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CBr}_3$, crystallises in needles melting at 187 — 190° . *p*-Dibenzylbenzene is best prepared by condensing formaldehyde with benzene, using ethyl acetate as the solvent; by the action of bromine in chloroform, *diphenyl-p-xylene bromide* is formed, which, after repeated crystallisation, melts at 112.5° . Silver or mercury act on this, forming yellow solutions which undoubtedly contain *diphenyl-p-xylene*, $\text{CHPh} \cdot \text{C}_6\text{H}_4 \cdot \text{CHPh}$, but this could not be isolated.

Tetraphenyl p-xyleneglycol dimethyl ether,

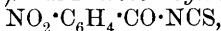


prepared by the interaction of magnesium phenyl bromide and methyl terephthalate, melts at 181 — 182.5° ; by bromine in acetic acid solution, it is converted into *tetraphenyl-p-xylene bromide*, $\text{CPh}_2\text{Br} \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}_2\text{Br}$, which crystallises in colourless plates, melts and decomposes at 270 — 272° , and dissolves in concentrated sulphuric acid with a deep orange coloration.

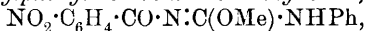
The hydrocarbon, *tetraphenyl-p-xylene* (1:4-bisdiphenylmethylene- $\Delta^{2,5}$ -cyclohexadiene), $\text{CPh}_2 \cdot \text{C} \begin{smallmatrix} \text{CH} \cdot \text{CH} \\ \text{CH} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{CPh}_2$, is prepared by boiling the bromide with silver in benzene solution in the dark. It forms glistening, orange-yellow needles, melts and decomposes at 239 — 242° , is sparingly soluble in all solvents, forms yellow or orange solutions which have a golden-yellow fluorescence and rapidly become colourless when exposed to light. It takes up bromine instantaneously, is rapidly reduced by aluminium amalgam, and liberates iodine from hydrogen iodide.

E. F. A.

Oxygen Ethers of Carbamides. W. M. BRUCE (*J. Amer. Chem. Soc.*, 1904, 26, 419—436).—*m*-Nitrobenzoylthiocarbimide,



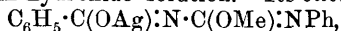
obtained by the action of *m*-nitrobenzoyl chloride on lead thiocyanate, melts at 94° . When heated with methyl alcohol, it is converted into *methyl m-nitrobenzoyliminothiocarbonate*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{N} \cdot \text{C}(\text{SH}) \cdot \text{OMe}$, which forms yellow crystals and melts at 120° ; its potassium salt decomposes at about 260° . *Methyl ethyl m-nitrobenzoyliminothiocarbonate*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{N} \cdot \text{C}(\text{SEt}) \cdot \text{OMe}$, crystallises in needles and melts at 78° . If this compound is treated with aniline, mercaptan is evolved and *s-m-nitrobenzoylphenylisocarbamide methyl ether*,



is produced, which crystallises in colourless needles and melts at 124° . The last-mentioned substance is more readily prepared by the action of *m*-nitrobenzoyl chloride on phenylisocarbamide methyl ether. When heated with dry hydrogen chloride, it suffers decomposition with formation of methyl chloride and *s-m-nitrobenzoylphenylcarbamide*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NHPh}$, which crystallises in colourless needles, melts at 224° , and is soluble in hot water. When the methyl ether of *m-nitrobenzoylphenylisocarbamide* is boiled with solution of potassium hydroxide, the free isocarbamide is not obtained, but decomposition occurs with production of *m*-nitrobenzoic acid and aniline.

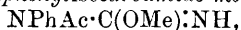
s-Benzoylphenylisocarbamide methyl ether, $\text{NBz} \cdot \text{C}(\text{OMe}) \cdot \text{NHPh}$,

crystallises in slender needles, melts at 50° , and is completely decomposed by boiling potassium hydroxide solution. Its *silver* derivative,



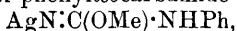
was prepared and analysed. The *hydrochloride* of benzoylisocarbamide methyl ether, $\text{NHbz} \cdot \text{C}(\text{OMe}) : \text{NH} \cdot \text{HCl}$, is unstable, and gradually undergoes decomposition with loss of methyl chloride; the *sodium* salt, $\text{C}_6\text{H}_5 \cdot \text{C}(\text{ONa}) : \text{N} \cdot \text{C}(\text{OMe}) : \text{NH}$, was also prepared.

By the action of acetyl chloride on phenylisocarbamide methyl ether, a mixture of isomeric acetyl derivatives is produced. *s*-Acetylphenylisocarbamide methyl ether, $\text{NHAc} \cdot \text{C}(\text{OMe}) : \text{NPh}$, is obtained as an oil, which is decomposed by dry hydrogen chloride with formation of methyl chloride and *s*-acetylphenylcarbamide; its *platinichloride* was prepared and analysed. *as*-Acetylphenylisocarbamide methyl ether,



crystallises in long, rhombic prisms, melts at 102° , and is readily soluble in chloroform, benzene, alcohol, acetone, or ether; it slowly undergoes rearrangement into the *s*-isomeride, and is readily hydrolysed with formation of phenylisocarbamide methyl ether; its *hydrochloride* was prepared and analysed. When the *as*-compound is treated with dry hydrogen chloride, methyl chloride is evolved and *as*-acetylphenylcarbamide, $\text{NPhAc} \cdot \text{CO} \cdot \text{NH}_2$, is produced, which crystallises from hot water in slender needles and melts at 167° .

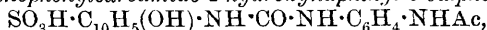
When the *silver* salt of phenylisocarbamide methyl ether,



is treated with acetyl bromide, *s*-acetylphenylcarbamide methyl ether is produced. The *silver* salts of phenylisocarbamide ethyl ether, *s*-acetylphenylisocarbamide methyl ether, and acetylisocarbamide methyl ether were also prepared.

Acetylisocarbamide methyl ether, $\text{NAc} : \text{C}(\text{OMe}) \cdot \text{NH}_2$, crystallises from light petroleum and melts at 58.5° . *m*-Nitrobenzoylisocarbamide methyl ether, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} : \text{N} \cdot \text{C}(\text{OMe}) \cdot \text{NH}_2$, crystallises in slender needles and melts at 115° . E. G.

p-Acetylaminophenylcarbamidohydroxynaphthylsulphonic Acid. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 148505).—When phosgene gas is passed into a solution of 6-amino- α -naphthol-3-sulphonic acid, *p*-aminoacetanilide, and sodium acetate, 6-*p*-acetylaminophenylcarbamido-1-hydroxynaphthyl-3-sulphonic acid,



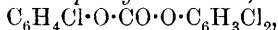
is formed as a greyish-white powder, dissolving sparingly in cold, readily in hot water, and precipitated from its alkaline solutions by dilute acids. It combines with solutions of diazonium salts to form orange azo-compounds, which are hydrolysed by dilute sodium hydroxide. C. H. D.

Viscosity of Mixtures of Water and Phenol. OSCARRE SCARPA (*Nuovo Cimento*, 1903, [v], 6, 277—288. Compare Abstr., 1903, ii, 640).—The author has made measurements of the viscosity of mixtures of water and phenol of various compositions at five different temperatures ranging from 67.5° to 85° , and has constructed the corresponding viscosity-composition curves. All these curves show two changes of

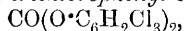
curvature at the points corresponding with about 58 and 15 per cent. respectively of phenol in the solution. T. H. P.

Action of Sulphur and of Selenium on the Organo-magnesium Compounds of Mono- and Di-halogenated Aromatic Hydrocarbons. F. TABOURY (*Compt. rend.*, 1904, 138, 982—983).—In addition to the thiophenols and disulphides already described (compare Abstr., 1903, i, 748), prepared by the interaction of sulphur and an aryl magnesium haloid, the following have also been obtained: from bromophenyl magnesium bromide, thiobromophenol and bromophenyl disulphide; from chlorophenyl magnesium bromide, thiochlorophenol and chlorophenyl disulphide; from bromonaphthyl magnesium bromide, thiobromonaphthol and bromonaphthyl disulphide; from chloronaphthyl magnesium bromide, thiochloronaphthol and chloronaphthyl disulphide. By the interaction of the above organo-magnesium compounds and benzoyl chloride, the following thiobenzoates have been obtained: *bromonaphthyl thiobenzoate*, $C_{10}H_6Br \cdot S \cdot COPh$, melting at $120-121^\circ$; *chloronaphthyl thiobenzoate*, $C_{10}H_6Cl \cdot S \cdot COPh$, melting at $111-112^\circ$; *bromophenyl thiobenzoate*, $C_6H_4Br \cdot S \cdot COPh$, melting at $83-84^\circ$, and *chlorophenyl thiobenzoate*, $C_6H_4Cl \cdot S \cdot COPh$, melting at $75-76^\circ$. M. A. W.

Chlorination of Phenyl Carbonate in the presence of Iodine. ÉTIENNE BARRAL (*Compt. rend.*, 1904, 138, 909—911).—All the chloro-derivatives of phenyl carbonate can be obtained either by direct chlorination of phenyl carbonate in the presence of a chlorine carrier, such as iodine, aluminium chloride, antimony pentachloride, or ferric chloride under suitable conditions of temperature (compare Abstr., 1898, i, 575) or synthetically from phosgene gas and the chlorinated phenols (compare Abstr., 1899, i, 747; 1901, i, 28). By the first method, and using iodine as a chlorine carrier, the following derivatives were obtained: (1) at the ordinary temperature or at 90° , phenyl *p*-chlorophenyl carbonate, $OPh \cdot CO \cdot O \cdot C_6H_4Cl$, melting at $95-96^\circ$ and crystallising in white, silky, pearly needles (compare Morel, *Thèse de Paris*, 1900); *p*-chlorophenyl carbonate, $CO(O \cdot C_6H_4Cl)_2$, melting at $144-145^\circ$ and not at 142° as stated in the earlier paper; (2) at 140° , *p*-chlorophenyl 2 : 4-(?)-dichlorophenyl carbonate,



crystallising in white, pearly needles melting at 115° , a small quantity of an isomeride melting at about 100° , and two isomeric 2 : 4-dichlorophenyl carbonates, $CO(O \cdot C_6H_3Cl_2)_2$, one (α -) melting at $122-123^\circ$, and the other (β -) melting at $88-89^\circ$; (3) at $150-155^\circ$, and by continuing the chlorination for a month, a mixed *di*- and *tri*-chlorophenyl carbonate, $C_6H_3Cl_2 \cdot O \cdot CO \cdot O \cdot C_6H_2Cl_3$, crystallising in white needles and melting at 94° , and 2 : 4 : 6-trichlorophenyl carbonate,



forming cauliflower-like clusters of hard needles melting at $153-154^\circ$, and less soluble than the preceding. M. A. W.

Chlorination of Phenyl Carbonate in the presence of Antimony Chloride. ÉTIENNE BARRAL (*Compt. rend.*, 1904, 138, 980—982).—In the presence of iodine, the chlorination of phenyl car-

bonate cannot be carried farther than the trichloro-derivative (compare preceding abstract), and attempts to prepare the higher derivatives by using aluminium chloride instead of iodine as a chlorine carrier were unsuccessful owing to the decomposition which occurred at the high temperature. In the presence of antimony chloride, however, at temperatures varying between 90° and 200°, in addition to the derivatives already obtained by the use of iodine, the following higher chlorinated derivatives of phenyl carbonate have been prepared: (1) a mixed *di*- and *tri*-chlorophenyl carbonate, $C_6H_3Cl_2 \cdot O \cdot CO \cdot O \cdot C_6H_2Cl_3$, crystallising in white needles melting at 130°; (2) 2 : 4 : 6-trichlorophenyl 2 : 3 : 4 : 6-tetrachlorophenyl carbonate, $C_6H_2Cl_3 \cdot O \cdot CO \cdot O \cdot C_6HCl_4$, crystallising in white, pearly needles melting at 175—176°; (3) 2 : 3 : 4 : 6-tetrachlorophenyl carbonate, $CO(O \cdot C_6HCl_4)_2$, crystallising in cauliflower-like clusters of pearly needles melting at 155—156°, also obtained synthetically from phosgene and potassium tetrachlorophenoxide; (4) 2 : 3 : 4 : 6-tetrachlorophenyl pentachlorophenyl carbonate $C_6HCl_4 \cdot O \cdot CO \cdot O \cdot C_6Cl_5$, forming white needles melting at 168—169°, and (5) pentachlorophenyl carbonate $CO(O \cdot C_6Cl_5)_2$, crystallising in white, translucent prisms melting at 258°, almost insoluble in neutral solvents, slightly soluble in cold benzene, more so on boiling; this compound has also been synthesised from phosgene and potassium pentachlorophenate.

M. A. W.

Derivatives of β -Amino-ornicinol. FERDINAND HENRICH, W. MEYER, and KARL DORSCHKY (*Ber.*, 1904, 37, 1425—1428. Compare Abstr., 1903, i, 413).— β -Amino-ornicinol picrate, $C_{13}H_{12}O_9N_4$, crystallises from hot aqueous solutions in greenish-yellow needles containing $1H_2O$, which it loses at 105°. It darkens at 140° and begins to decompose at 190°. The acid sulphate, $C_8H_9O_2N \cdot H_2SO_4$, is sparingly soluble in water. The ferrocyanide, $4C_7H_9O_2N \cdot H_4FeC_6N_6$, forms a brown precipitate. The normal oxalate crystallises in needles. Bromine reacts with an acetic acid solution of the hydrochloride yielding a dibromo-derivative, the hydrochloride of which is sparingly soluble in cold water and may be crystallised from glacial acetic acid. The dibromo-hydrochloride, on treatment with acetic anhydride and subsequent hydrolysis with alcoholic potash, yields 4 : 6-dibromo-5-

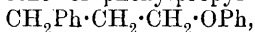
hydroxy-1 : 3-dimethylbenzoxazole,
$$\begin{array}{c} OH \cdot C \equiv CBr \cdot \overset{\overset{O}{\parallel}}{C} \cdot O \\ | \qquad \qquad \qquad | \\ CBr \cdot CMe \cdot \overset{\overset{O}{\parallel}}{C} \cdot N \end{array} \gg CMe$$
, melting at 221—222° and only sparingly soluble in ether or light petroleum.

Hypochlorous acid transforms β -amino-ornicinol hydrochloride into a compound $C_7H_7O_4Cl_3$, which crystallises in needles and melts at 97°. It dissolves in alkalis. A second compound $C_7H_6O_4Cl_2$, melting at 117°, is also formed.

J. J. S.

Action of Magnesium and Organo-magnesium Compounds on Bromophenetole. VICTOR GRIGNARD (*Compt. rend.*, 1904, 138, 1048—1050. Compare Abstr., 1902, i, 142, 198, 420; 1903, i, 31, 141, 455, 549, 552; this vol., i, 213; Hamonet, this vol., i, 401).—Bromophenetole reacts with magnesium on warming in the presence of dry ether to form ethylene and a crystalline derivative which, on hydrolysis, furnishes phenol; probably the normal magnesium compound is first formed, and breaks down

according to the equation $\text{OPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{MgBr} = \text{OPh}\cdot\text{MgBr} + \text{CH}_2\cdot\text{CH}_2$. A small quantity of $\alpha\delta$ -diphenoxybutane, $\text{C}_4\text{H}_8(\text{OPh})_2$, crystallising in plates melting at 98° , is also formed. Bromophenetole reacts abnormally with magnesium amyl bromide to form phenol and amyl alcohol, and normally with magnesium phenyl bromide, giving a little phenol and 83 per cent. of the phenyl ether of benzylcarbinol, $\text{OPh}\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$ (compare Abstr., 1903, i, 819; and Tiffeneau and Delange, this vol., i, 48), which is a liquid boiling at 166° under 14 mm. pressure, and converted by heating with hydrobromic acid in an autoclave at 120° into β -phenylethyl bromide, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\text{Br}$, boiling at 92° under 11 mm., and at $217\text{--}218^\circ$ under 734 mm. pressure, and reacting with magnesium to form the normal magnesium derivative together with a little styrene and diphenylbutane; the magnesium derivative reacts with carbon dioxide to form phenylpropionic acid melting at 48° (50 per cent.), and is oxidised by a current of oxygen giving benzylcarbinol (60 per cent.) boiling at 102° under 13 mm. and 220° under 750 mm. pressure (compare Tiffeneau and Delange, this vol., i, 48). Bromophenetole reacts with magnesium benzyl chloride at 100° to form phenol, benzyl alcohol, and a small quantity of the phenyl ether of phenylpropyl alcohol,



which boils at $171\text{--}172^\circ$ under 11 mm. pressure, yields β -phenylpropyl bromide, boiling at 110° under 12 mm. pressure, the constitution of which has been established by the formation of phenylbutyric acid, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, melting at $47\text{--}48^\circ$, by the action of carbon dioxide on the magnesium derivative. M. A. W.

Condensation Products of Aldehydes of the Aliphatic Series with Phenol. A. I. LUNJAK (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 301—311).—The *di-p-methoxydiphenylethane*, $\text{C}_2\text{H}_4(\text{C}_6\text{H}_4\cdot\text{OMe})_2$, prepared by the action of potassium hydroxide and methyl iodide on a methyl-alcoholic solution of *di-p-hydroxydiphenylethane*, crystallises from ether in plates melting at 59.4° and boiling at $352\text{--}354^\circ$ under 767 mm. pressure. On oxidation with chromic anhydride in acetic acid solution, it yields *di-p-methoxybenzophenone*, anisic acid, and *p*-acetylanisole. From these results, the author concludes that the structure of dihydroxydiphenylethane is $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHMe}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, the hydroxyl groups being in the para-positions to the central carbon atom.

Di-p-hydroxydiphenylheptane, $\text{C}_7\text{H}_{14}(\text{C}_6\text{H}_4\cdot\text{OH})_2$, prepared by the condensation of cenanthaldehyde and phenol, separates from light petroleum in pale yellow, microscopic, rhombic plates melting at 103° . Its *dibenzoyl* derivative, $\text{C}_7\text{H}_{14}(\text{C}_6\text{H}_4\cdot\text{OBz})_2$, is deposited from dilute alcohol in star-shaped aggregates of microscopic, acicular crystals melting at 106° . The *dimethyl ether*, $\text{C}_7\text{H}_{14}(\text{C}_6\text{H}_4\cdot\text{OMe})_2$, is a liquid of sp. gr. 1.02496 at $15^\circ/4^\circ$, and, on oxidation with chromic anhydride in acetic acid, yields *p*-dimethoxybenzophenone and anisic acid. T. H. P.

Action of Dilute Nitric Acid on Haloid Compounds. MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 220—223).—The

author's investigations on the action of dilute nitric acid on halogen compounds of various types lead to the following conclusions: (1) the haloid compounds of saturated character enter into reaction with dilute nitric acid more readily than the corresponding hydrocarbons. (2) The primary and secondary haloid compounds yield either nitro-products or oxidation products, in both cases containing halogens. The readiness of formation and character of the nitro-compounds formed under these conditions varies with the structure of the hydrocarbon radicle. (3) Tertiary, non-aromatic, haloid compounds, under the action of dilute nitric acid, very readily give up hydrogen haloid, forming unsaturated hydrocarbons which may then undergo nitration.

T. H. P.

Action of Nitric Acid on Alcohols. II. MICHAEL I. KONOWALOFF and N. MANEWSKY (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 224—227. Compare Abstr., 1901, i, 249).—The action of dilute nitric acid on benzyldimethylcarbinol leads first to the removal of water from, and oxidation of, the alcohol, yielding benzaldehyde and benzoic acid; this result would be expected, supposing that the nitric acid acts most rapidly on the carbon group combined immediately with the phenyl. The oxime and secondary nitro-compound also probably result from this action of nitric acid. This removal of water by dilute nitric acid is evidently a general reaction for tertiary alcohols, with the exception of phenols. A similar action is evidenced between dilute nitric acid and tertiary haloid compounds (see preceding abstract). Simultaneously with the removal of water from the alcohol proceeds the nitration of the unsaturated hydrocarbon thus formed. The formation of the primary nitro-compound obtained in this way confirms the views of Konowaloff on the nitration of unsaturated hydrocarbons (*J. Russ. Phys. Chem. Soc.*, 1894, 26, 382). T. H. P.

Synthesis of Alcohols by means of Organo-magnesium Compounds. II. MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 228—232. Compare Abstr., 1902, i, 336).—Other alcohols prepared by the author by Grignard's method (Abstr., 1900, i, 382) are the following:

Benzyldimethylcarbinol (compare Grignard, Abstr., 1901, i, 679), which boils at 214—216° at the ordinary pressure, and has the sp. gr. 0.9823 at 15°/0° and n_D 1.5201 at 15°.

Benzyl-diethylcarbinol, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{Et})_2\cdot\text{OH}$, obtained from magnesium benzyl chloride and diethyl ketone, boils at 245°.

Benzylmethyl-ethylcarbinol, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{MeEt})\cdot\text{OH}$, prepared from magnesium benzyl chloride and methyl ethyl ketone, boils, decomposing slightly, at 235—238°, has the sp. gr. 0.9927 at 0°/0° and 0.9754 at 20°/0° and n_D 1.51817 at 20°.

Methylethyl-isoamylcarbinol, $\text{C}_5\text{H}_{11}\cdot\text{C}(\text{MeEt})\cdot\text{OH}$, obtained from magnesium isoamyl chloride and methyl ethyl ketone, boils at 174—176° and has the sp. gr. 0.8286 at 16°/0° and n_D 1.43256 at 16°.

The formation of certain other products in the preparation of alcohols by this method is regarded by the author as due to the action

exerted on the organo-magnesium compounds by the oxygen of the air (Abstr., 1903, i, 249).
T. H. P.

Styrenes. V. AUGUST KLAGES (*Ber.*, 1904, 37, 1721—1726. Compare this vol., i, 302).—The aryl group affects the reduction of Δ^{α} -styrenes in the same way as the carboxylic group does the reduction of $\alpha\beta$ -unsaturated acids, thus the Δ^{α} -styrenes, corresponding in constitution to $\alpha\beta$ -unsaturated acids, which are reduced with difficulty, are not reduced by sodium and alcohol; the effect of the aryl group is modified by the presence of substituting groups. The formation of Δ^{α} -styrenes from β -halogenated benzene hydrocarbons is to be compared to the formation of $\alpha\beta$ -unsaturated acids from β -halogen substituted acids.

[With HUGO HAEN.]—Benzylidimethylcarbinol, $\text{CH}_2\text{Ph}\cdot\text{CMe}_2\cdot\text{OH}$, prepared by acting with magnesium and methyl iodide on ethyl phenylacetate, forms long, glistening needles, melts at 24° to a viscid, colourless oil, boils at $127\text{--}128^\circ$ under 14 mm. pressure, and has a sp. gr. 0.9774 at $19^\circ/4^\circ$; the *phenylurethane* forms long needles and melts at 96° ; the *chloride* is an oil which, when heated with pyridine at 125° , forms β -methyl- Δ^{α} -propenylbenzene, $\text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{CMe}_2$, which boils at $76\text{--}77^\circ$ under 14 mm., at $181\text{--}182^\circ$ under 761 mm. pressure, has a sp. gr. 0.9022 at $14.5^\circ/4^\circ$, and n_D 1.5280, and is not reduced by sodium and alcohol.

Benzylidiethylcarbinol, $\text{CH}_2\text{Ph}\cdot\text{CEt}_2\cdot\text{OH}$, is a viscid, odourless oil, that boils at 135° under 16 mm., at $243\text{--}245^\circ$ under 755 mm. pressure, and has a sp. gr. 0.9782 at $19^\circ/4^\circ$; the *phenylurethane* melts at 98° ; the *chloride* is an oil with a strong odour; when heated, it loses hydrogen chloride. β -Ethyl- Δ^{α} -butenylbenzene, $\text{CHPh}\cdot\text{CEt}_2$, is a mobile oil, which boils at $97\text{--}98^\circ$ under 13 mm. pressure, at $204\text{--}206^\circ$ with slight decomposition, has a sp. gr. 0.9038 at $18.5^\circ/4^\circ$ and n_D 1.5182 at 18.5° ; it is not reduced by sodium and alcohol. The *dibromide* is an oil, the nitrosyl chloride melts at 99° .

Phenylethylisopropylcarbinol, $\text{OH}\cdot\text{CEtPh}\cdot\text{Ph}$, obtained from ethyl iodide and butyrylbenzene, boils at $114\text{--}116^\circ$ under 18 mm. pressure, at $224\text{--}226^\circ$ with decomposition, has a sp. gr. 0.9689 at $12.5^\circ/4^\circ$ and n_D 1.5155; the *chloride* is a mobile oil. β -Methyl- α -ethyl- Δ^{α} -propenylbenzene, $\text{CEtPh}\cdot\text{CMe}_2$, boils at $83\text{--}84^\circ$ under 15 mm., at $206\text{--}207^\circ$ under 765 mm. pressure, has a sp. gr. 0.8913 at $14.5^\circ/4^\circ$ and n_D 1.5134, and forms a *dibromide*. The hydrocarbon is very slightly reduced by sodium and alcohol; the product boils at $81\text{--}82^\circ$ under 12 mm. pressure and has a sp. gr. 0.8851 at 15° .

Phenylpropylisopropylcarbinol, obtained from magnesium propyl iodide and isobutyrylbenzene, boils at $116\text{--}117^\circ$ under 13 mm., at $230\text{--}232^\circ$ under 759 mm. pressure, and has a sp. gr. 0.9681 at $19^\circ/4^\circ$. The *chloride* is a mobile oil.

β -Methyl- α -propyl- Δ^{α} -propenylbenzene, $\text{CPhPr}\cdot\text{CMe}_2$, boils at $94\text{--}96^\circ$ under 12 mm., at $210\text{--}212^\circ$ under 755 mm. pressure, has a sp. gr. 0.8897 at $16^\circ/4^\circ$, n_D 1.5070 at 16° , and is not reduced by sodium and alcohol. The *dibromide* is an oil.
G. Y.

The Parent Carbinol of Rosaniline and its Isomerides. AUGUSTIN BISTRZYCKI and JOSEPH GYR (*Ber.*, 1904, 37, 1245—1253. Compare this vol., i, 315, and Acree, *ibid.*, i, 315, 409).—*Diphenyl-*

o-tolylcarbinol, $C_6H_4Me \cdot CPh_2 \cdot OH$, prepared by the action of magnesium phenyl bromide on methyl *o*-toluate, separates from alcohol in snow-white crystals and melts at 98° ; on reduction with zinc and glacial acetic acid, it is converted into *diphenyl-o-tolylmethane*, which crystallises from methyl alcohol in well-formed, six-sided prisms and melts at $82-83^\circ$. Hemilian's diphenyl-*o*-tolylmethane (m. p. 62°) (Abstr., 1884, 322) is really identical with O. and E. Fischers' diphenyl-*m*-tolylmethane melting at $59-59.5^\circ$. *Diphenyl o-tolylchloromethane*, $C_6H_4Me \cdot CPh_2Cl$, prepared by the action of hydrogen chloride on the carbinol in ethereal solution, crystallises in prisms and melts at $136-137^\circ$.

Diphenyl-m-tolylcarbinol, prepared from methyl *m*-toluate, crystallises from benzene in six-sided, colourless leaflets, melts at $67-68^\circ$, and is not identical with the Fischers' diphenyl-*m*-tolylcarbinol, which melts at 150° (Abstr., 1879, 386), although, on reduction with zinc and acetic acid, it gives the same diphenyl-*m*-tolylmethane melting at $60.5-61.5^\circ$ as was obtained by them. On oxidising the hydrocarbon with chromic acid in glacial acetic acid solution, the diphenyl-*m*-tolylcarbinol (m. p. $67-68^\circ$) was regenerated. The nature of the Fischers' carbinol is being investigated.

W. A. D.

Compounds of Amino-carboxylic Esters with Aromatic Sulphonic Acids. EDUARD RITSERT (D.R.-P. 149345 and 150070. Compare this vol., i, 413).—In place of phenolsulphonic acids, the sulphonic acids of phenyl ethers may be combined with amino-carboxylic esters to form soluble salts. Anisolesulphonic acid and ethyl *p*-aminobenzoate combine to form a salt $OMe \cdot C_6H_4 \cdot SO_3H, NH_2 \cdot C_6H_4 \cdot CO_2Et$, which crystallises in glistening needles, melts at 188° , and dissolves readily in hot water or alcohol. The salt from guaiacolsulphonic acid and ethyl *p*-aminobenzoate crystallises in needles and melts at 175° .

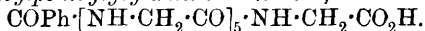
p-Amino-carboxylic esters also form soluble salts with the benzenesulphonic acids. Ethyl *p*-aminobenzoate toluene-*p*-sulphonate forms prismatic crystals and melts at $185-187^\circ$. Ethyl *p*-aminobenzoate benzene-*m*-disulphonate, $2NH_2 \cdot C_6H_4 \cdot CO_2Et, C_6H_4(SO_3H)_2$, forms coarse crystals and decomposes at 235° . Methyl *m*-amino-*p*-hydroxybenzoate benzene-*m*-disulphonate forms slender needles and melts and decomposes at 142° .

C. H. D.

Conversion of Anthranilodiacetic Acid into Phenylglycine-*o*-carboxylic or Anthranilic Acids. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 149346).—Small quantities of anthranilodiacetic acid, $CO_2H \cdot C_6H_4 \cdot N(CH_2 \cdot CO_2H)_2$, are always obtained in the preparation of phenylglycine-*o*-carboxylic acid from anthranilic acid and chloroacetic acid. It is not readily convertible directly into indoxyl or indoxyllic acid, but may be converted by acid, neutral, or alkaline oxidising agents into phenylglycine-*o*-carboxylic acid. It is not always possible to stop the reaction at this stage, and a portion is then further oxidised to anthranilic acid, which may be reconverted into phenylglycine-*o*-carboxylic acid by the action of chloroacetic acid.

C. H. D.

Benzoylpentaglycyclaminoacetic Acid. THEODOR CURTIUS and A. BENRATH (*Ber.*, 1904, 37, 1279—1284).—The so-called “ γ -acid” obtained by Curtius (*Abstr.*, 1883, 337) as the final product of the action of benzoyl chloride on silver glycine, and also by fusing ethyl hippurate with glycine, is best prepared by the latter method, and proves to be *benzoylpentaglycyclaminoacetic acid*,



It crystallises from hot water and melts at 280—285°. Concentrated hydrochloric acid hydrolyses it at 100° to benzoic acid and glycine hydrochloride. The *silver* salt forms a bulky precipitate. The *ethyl* ester forms a loose powder and melts and decomposes at 263°. H. Levy has obtained the same ester synthetically from benzoyltriglycyclaminoacetic azoimide (Curtius, *Abstr.*, 1902, i, 844) and ethyl glycyglycine (E. Fischer, *Abstr.*, 1901, i, 675).

The mother-liquor from the preparation of the acid, contains benzoyltriglycyclaminoacetic acid, ethyl hippurate, and hippurylaminoacetic acid.
C. H. D.

Preparation of Phenyl Ether-*o*-carboxylic Acid. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 150323).—Phenyl ether-*o*-carboxylic acid (Graebe, *Abstr.*, 1888, 477) is readily prepared by heating phenol with salts of *o*-chlorobenzoic acid in the presence of copper or of copper salts.
C. H. D.

Acids obtained on Nitration with Dilute Nitric Acid.
I. **3-Methyl-5-*tert*-Butylbenzoic Acid (1:3:5).** MICHAEL I. KONOWALOFF and ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 232—237).—The oxidation of *tert*-butylxylene by means of dilute nitric acid yields 3-methyl-5-*tert*-butylbenzoic acid (compare Baur-Thurgau, *Abstr.*, 1898, i, 523). The *copper* (+2H₂O) and *barium* salts were prepared and also the *ethyl* ester, which boils at 268—270° under 743 mm. pressure, has the sp. gr. 0.9896 at 23°/0° and n_D 1.50139 at 23°. T. H. P.

Two Isomeric β -Methylcinnamic Acids. MARC TIFFENEAU (*Compt. rend.*, 1904, 138, 985—987. Compare Schroeter, this vol., i, 415).—Owing to the readiness with which the two isomeric β -methylcinnamic acids (compare *Abstr.*, 1903, i, 241) are hydrogenated to form the corresponding saturated acid, it is probable that the isomerism is stereomeric. The two acids are readily separated owing to the difference of their solubilities in light petroleum or carbon disulphide, and they melt at 129° and 97—98° respectively. The acid melting at 129° distils without decomposition at 170—172° under 14 mm. pressure, yields methylstyrene when heated with barium hydroxide, and is readily hydrogenated by hydrogen iodide in the presence of phosphorus.

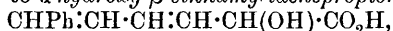
The acid melting at 97—98°, also prepared by saponifying the ethyl methylcinnamate obtained by the condensation of acetophenone and ethyl iodoacetate in the presence of magnesium, distils without decomposition at 171—174° under 15 mm. pressure, yields α -methyl-

styrene when heated with barium hydroxide, and is hydrogenated by hydrogen iodide in the presence of phosphorus to form a saturated acid boiling at 274—276°; the *methyl* ester boils at 259—260°, forms leafy crystals from alcohol, melting at 28° and having a sp. gr. 1.055 at 28°; the *ethyl* ester boils at 269—271° and has a sp. gr. 1.041 at 19°; the anilide (compare Henrich and Wirth, this vol., i, 431) melts at 121°.

M. A. W.

Conversion of Cinnamylidenepyruvic Acid into δ -Benzylidenelævulic Acid. EMIL ERLNMEYER, jun. (*Ber.*, 1904, 37, 1318—1322).—The reduction of cinnamylformic acid to α -hydroxy- γ -phenylisocrotonic acid (Abstr., 1903, i, 698) is remarkable, since other similar acids undergo reduction at the double linking. Cinnamylidenepyruvic acid behaves like cinnamylformic acid.

Cinnamylidenepyruvic acid, $\text{CHPh}:\text{CH}:\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{CO}_2\text{H}$, prepared by condensing pyruvic acid and cinnamaldehyde with sodium hydroxide, crystallises from water in orange needles containing H_2O and melts at 75°; it becomes yellow on drying in a vacuum and then melts at 107°. Sodium amalgam and glacial acetic acid reduce its alcoholic solution to α -hydroxy- β -cinnamylidenepropionic acid,



crystallising from benzene in yellow needles and melting at 145°. Boiling with dilute hydrochloric acid converts it into δ -benzylidenelævulic acid (Erdmann, Abstr., 1890, 495).

C. H. D.

Preparation of Indigotin. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 149638).—The leuco-compounds obtained by fusing phenylglycine and its derivatives with alkali amides (D.R.-P. 137955) are only imperfectly oxidised to indigo dyes on dissolving in water and passing a current of air, a considerable part being always converted into red dyes, which are partially soluble in dilute acids. If sodium nitrate is added to the solution (25 kilos. to the mass obtained from 300 kilos. of phenylglycine salt), the oxidation to indigotin or its derivatives is practically complete.

C. H. D.

Preparation of Bromoindigotin. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 149941 and 149989).—The action of bromine on a 10 or 20 per cent. indigo paste produces very little bromoindigotin, only bromoisatin and other decomposition products being obtained. The action of liquid or gaseous bromine on indigotin which is only moistened with water, however, yields bromoindigotin. A similar product is obtained by the bromination of indigotin in presence of concentrated hydrochloric or hydrobromic acid, with or without the addition of a carrier, such as ferrous chloride. The hydrobromic acid produced may be utilised by adding hypochlorites, &c., thus rendering the bromine again available. It has not been determined whether the products are identical with the bromoindigotins prepared synthetically from indoxyl.

C. H. D.

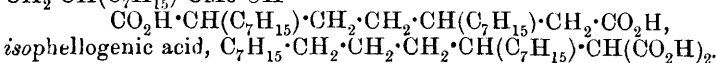
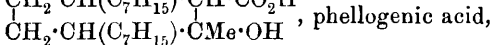
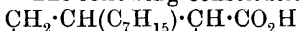
Cork. I and II. MAX VON SCHMIDT (*Monatsh.*, 1904, 25, 277—301, 302—310).—Kügler's formula, $C_{22}H_{42}O_3$, for phellonic acid is to be preferred to Gilson's, $C_{22}H_{44}O_3$ (*Abstr.*, 1891, 465). When boiled with acetic anhydride, phellonic acid yields an acetyl derivative, $C_{22}H_{41}O_3Ac$, which melts at 80° . With hydriodic acid, phellonic acid yields *iodophellanic acid*, $C_{22}H_{41}O_3I$, which, again, by boiling potassium hydroxide solution, is converted into phellonic acid. When treated with zinc and alcoholic hydrochloric acid, *iodophellanic acid* yields *ethyl isophellonate*, $C_{22}H_{41}O_3Et$, which melts at $52-53^\circ$ and is hydrolysed by alcoholic potassium hydroxide, forming *isophellonic acid*, $C_{22}H_{42}O_3$. This melts at 73° and forms a soluble potassium salt. When heated with hydriodic acid and phosphorus, phellonic acid yields a soft, waxy substance, forming granular masses and melting at about 200° .

With bromine, phellonic acid forms a white, crystalline substance, which melts at $80-81^\circ$ and loses bromine when boiled with aqueous potassium hydroxide.

Fusion of phellonic acid with potassium hydroxide leads to the formation of *phellogenic acid*, $C_{21}H_{40}O_4$, which crystallises in slender needles and melts at 121° . This dibasic acid is also obtained by fusing cork meal with potassium hydroxide. *isoPhellogenic acid* is formed from phellonic acid by the action of warm concentrated nitric acid and acetic acid. It is crystalline and melts at 100° . The action of nitric acid alone on phellonic acid and on *isophellogenic acid* leads to the formation of suberic acid.

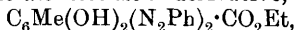
Gilson's violet iodine reaction and the violet coloration of cork by potassium hydroxide solution are not reactions for phellonic acid.

The following constitutional formulæ are suggested: phellonic acid,

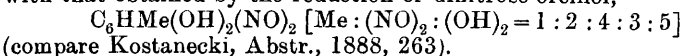


The chloroform extract of cork contains glycerides of fatty acids, cerin, and other substances, but the alcoholic potassium hydroxide extract, contrary to Kügler's statement, contains at most only traces of glycerides. G. Y.

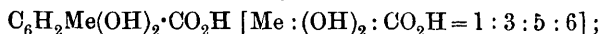
Constitution of Orsellinic Acid. FERDINAND HENRICH [and, in part, with KARL DORSCHKY] (*Ber.*, 1904, 37, 1406—1415).—Benzene-diazonium chloride (2 mols.) reacts with an alkaline solution of ethyl orsellinate yielding the *disazobenzene* derivative,



which crystallises from acetic acid in dark red needles containing 1 mol. of acetic acid, which they lose at 130° . It melts at 186° , has basic properties, and on reduction in alcoholic solution with stannous chloride and hydrochloric acid and further heating with hydrochloric acid at 160° yields a *diamino-orscinol hydrochloride*, identical with that obtained by the reduction of dinitroso-orscinol,



The constitution of orsellinic acid is thus



the dissociation constant, $K = 0.0127$, is in perfect harmony with this constitution.

Benzenediazonium chloride reacts with an alkaline solution of para-orsellinic acid yielding a brown product, which, on reduction, yields the isomeric 2:6-diamino-orscinol, which differs from the 2:4-compound in its colour reactions.

| | 2:4-Diamino- hydrochloride. | 2:6-Diamino- hydrochloride. |
|-----------------------|--------------------------------|--------------------------------|
| Ferric chloride | blue colour | red |
| Sodium hydroxide... | pale violet | yellowish-red |
| Dichromate | intense blue | red |
| Sodium nitrite | blue | brown and then dark green |
| Bleaching powder ... | blue, unstable. | precipitate, stable. |

J. J. S.

Derivatives of Ethyl Amino-orsellinate. Contribution to Formation of Litmus Dyes. FERDINAND HENRICH and KARL DORSCHKY (*Ber.*, 1904, 37, 1416—1424).—Ethyl orsellinate in alkaline solution reacts with benzenediazonium chloride (1 mol.) yielding *ethyl benzeneazo-orsellinate*, $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{C}_6\text{HMe}(\text{OH})_2\cdot\text{CO}_2\text{Et}$, in the form of dark orange-yellow needles melting at 142° , and soluble in alkalis and in concentrated sulphuric acid. On reduction with stannous chloride and hydrochloric acid in alcoholic suspension, it yields *ethyl amino-orsellinate hydrochloride* in the form of long, colourless needles decomposing at 236° . Its *tribenzoyl* derivative crystallises in small needles melting at 222.5° and is soluble in warm benzene, ethyl acetate, or acetone.

When heated with concentrated hydrochloric acid at 160° , the ethyl ester of the amino-acid is converted into β -amino-orscinol hydrochloride (*Abstr.*, 1903, i, 413) and must therefore have the constitution $[\text{CH}_3 : \text{CO}_2\text{Et} : (\text{OH})_2 : \text{NH}_2 = 1 : 2 : 3 : 5 : 6]$.

An alkaline solution of the ethyl ester of the amino-acid is oxidised by the atmospheric oxygen to an orange-coloured dye melting at 191 — 192° . Its solutions in alcohol, in ethyl acetate, or acetone fluoresce, but not the solutions in benzene, light petroleum, or carbon disulphide. It has basic properties.

Benzenediazonium chloride reacts with an alkaline solution of orsellinic acid yielding *benzeneazo-orsellinic acid*,

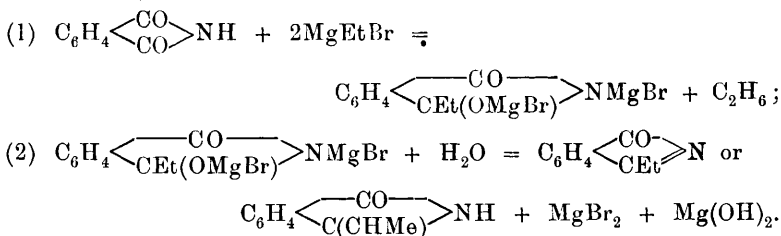


this decomposes at 191° and on reduction yields β -amino-orscinol.

p-Orsellinic acid and benzenediazonium chloride yield an *azo*-compound, $\text{C}_{14}\text{H}_{12}\text{O}_4\text{N}_2$, which crystallises from nitrobenzene in long, orange-yellow needles decomposing at 191° . It is far less soluble than its isomeride in the majority of solvents, and on reduction yields the *hydrochloride* of *amino-p-orsellinic acid* in the form of colourless needles.

J. J. S.

Action of Organo-magnesium Compounds on Phthalimide and Phenylphthalimide. CONSTANTIN BÈIS (*Compt. rend.*, 1904, 138, 987—989. Compare this vol., i, 15).—Phthalimide reacts with organo-magnesium compounds to yield derivatives of isoindole (isoindolones) according to the equations :



These compounds are crystalline, almost insoluble in water, soluble in the ordinary organic solvents, and crystallise well from acetic acid; *ethylisoindolone* melts at 210°, *isobutylisoindolone* at 180°, and *isoamylisoindolone* at 115°.

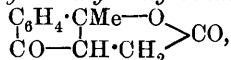
The reasons for assigning the above constitution to these compounds and not that of the isomeric ketonitrile, $\text{CN} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{R}$, are (1) the compounds give neither semicarbazones, phenylhydrazones, nor any colour reactions of ketones; (2) they are not reduced by sodium in alcoholic solution, or by zinc and acetic acid; (3) they do not give acids on boiling with alcoholic potassium hydroxide; (4) the melting point of *ethylisoindolone* is 210°, much higher than that of the corresponding acid, $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{COEt}$, which melts at 91°, whereas the nitrile usually has a lower melting point than the acid.

M. A. W.

Configuration of the Stereoisomeric Phenylmethylitaconic Acids. (Indoneacetic Acids. II.) HANS STOBBE [and, in part, ROBERT ROSE] (*Ber.*, 1904, 37, 1619—1624. Compare *Abstr.*, 1902, i, 542).—Concentrated sulphuric acid at 0° converts phenylmethylitaconic acid (melting at 183°) into a mixture of methylindoneacetic acid and hydroxymethylhydrindoneacetolactone.

3-Methyl-1-indone-2-acetic acid, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CMe} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{C} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, crystallises from benzene in small, yellow prisms, melts at 154—155°, and dissolves readily in alcohol, ether, chloroform, or acetic acid, more sparingly in benzene or light petroleum, very sparingly in water. It forms yellow alkali salts and dissolves in concentrated sulphuric acid to a violet solution, slowly becoming colourless. The *semicarbazone*, $\text{C}_{13}\text{H}_{13}\text{O}_3\text{N}_3$, forms bright yellow needles and melts and decomposes at 218—219°. Potassium permanganate oxidises the acid to phthalic acid.

The lactone of 3-hydroxy-3-methyl-1-hydrindone-2-acetic acid,

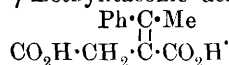


forms colourless, rhombic crystals, melts at 179.5°, and dissolves

sparingly in ether, more readily in alcohol or acetone. Bases form the yellow salts of methylindoneacetic acid, not the colourless salts of the hydroxy-acid. The *semicarbazone*, $C_{13}H_{13}O_3N_3$, forms white needles and melts and decomposes at 258—259°.

Phenylmethylitaconic acid, on treatment with cold concentrated sulphuric acid, yields phenylmethylitaconic anhydride only. The diethyl ester yields a mixture of the acid and anhydride.

The results prove that γ -phenyl- γ -methylisotaconic acid, melting at 183°, is the *cis*-modification, $\text{Ph} \cdot \overset{\text{C} \cdot \text{Me}}{\underset{|}{\text{C}}} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, and γ -phenyl- γ -methylitaconic acid, melting at 171°, is the *cis-trans*-modification,



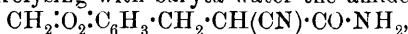
C. H. D.

General Method for Preparing Substituted Malonic Acids.
GALEAZZO PICCININI (*Atti R. Accad. Sci. Torino*, 1904, 39, 121—139).

—Aldehydes condense with cyanoacetamide according to the equation

$\text{R} \cdot \text{CHO} + \text{CN} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2 + \text{H}_2 = \text{R} \cdot \text{CH}_2 \cdot \text{CH}(\text{CN}) \cdot \text{CO} \cdot \text{NH}_2 + \text{H}_2\text{O}$, the hydrogen on the left hand side of the equation being supplied by the reacting substances; on hydrolysis, the resultant amide produces the acid $\text{R} \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{H})_2$.

Methylenedioxybenzylmalonic acid, $\text{CH}_2 \cdot \overset{\text{O}}{\underset{\text{O}}{\text{C}}} \cdot \text{C}_6\text{H}_3 \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{H})_2$, prepared by hydrolysing with baryta water the amide,

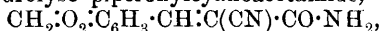


formed from the interaction of piperonaldehyde with ethyl cyanoacetate and ammonia, crystallises from water in hard, lustrous prisms and melts at 142—144°; the *barium* salt, $\text{C}_{11}\text{H}_8\text{O}_6\text{Ba} \cdot 3\text{H}_2\text{O}$, and the *calcium* salt, $\text{C}_{11}\text{H}_8\text{O}_6\text{Ca} \cdot \frac{1}{2}\text{H}_2\text{O}$, are crystalline. On heating the acid for several hours at 130°, it evolves carbon dioxide and is converted into methylenehydraccaffic acid, $\text{CH}_2 \cdot \text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ (Lorenz, *Abstr.*, 1881, 49). If the foregoing amide is hydrolysed with milk of lime instead of with baryta, *methylenedioxybenzylcyanoacetic acid*, $\text{CH}_2 \cdot \text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH}_2 \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{H}$, is obtained; it crystallises from ether in colourless needles or prisms and melts at 142°.

isoAmylmalonic acid, $\text{CH}_2 \cdot \text{P}i^{\beta} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{H})_2$, is prepared by hydrolysing *isoamylcyanoacetamide*, obtained by the interaction of *isovaleraldehyde* with ethyl cyanoacetate or cyanoacetamide in presence of ammonia; it separates from ether in small, hard crystals and melts at 98°.

n-Heptylmalonic acid, $\text{CH}_3 \cdot [\text{CH}_2]_6 \cdot \text{CH}(\text{CO}_2\text{H})_2$, prepared by hydrolysing *n-heptylcyanoacetamide* with baryta water, separates from benzene in lustrous, unctuous crystals, melts at 95°, and gives a micro-crystalline *barium* salt, $\text{C}_{10}\text{H}_{16}\text{O}_4\text{Ba} \cdot 3\text{H}_2\text{O}$. *n-Heptylcyanoacetic acid*, $\text{CH}_3[\text{CH}_2]_6 \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{H}$, is formed simultaneously in small quantity; it crystallises from ether and melts at 141°.

Attempts to hydrolyse piperonylcyanacetamide,



with aqueous barium hydroxide gave only piperonaldehyde and malonic acid, not piperonylmalonic acid, $\text{CH}_2 \cdot \text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH} \cdot \text{C}(\text{CO}_2\text{H})_2$;

the latter compound also could not be obtained by condensing together malonic acid and piperonaldehyde in presence of glacial acetic acid, piperonylacrylic acid being the sole product (compare Lorenz, *loc. cit.*).
W. A. D.

Polymeric Coumaric Acids. KNUT T. STRÖM (*Ber.*, 1904, 37, 1383—1386).—*o*-Coumaric acid and its alkyl derivatives polymerise on exposure to light, the original crystals falling to powder.

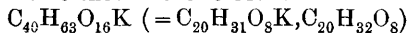
Bis-o-coumaric acid, $C_{18}H_{16}O_6$, crystallises from water and melts above 275° , decomposing at higher temperatures into coumarin and a compound not yet identified, which sublimes in leaflets. Boiling glacial acetic acid converts the acid into *biscoumarin*, which crystallises in small needles or leaflets and does not melt at 275° . It does not appear to be identical with Ciamician and Silber's polymeric coumarin (*Abstr.*, 1903, i, 171).

Bisethyl-o-coumaric acid melts at $273-274^\circ$, *bispropyl-o-coumaric acid* at 254° , *bisopropyl-o-coumaric acid* at 264° , and *bisallyl-o-coumaric acid* at 236° . The polymerisation of α -propylcoumaric acid was complete in 3 days, whilst the β -acid required 14 days. No polymerisation occurs in alcoholic solution.

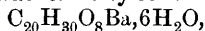
The polymeric acids are dibasic; they form calcium salts containing $5H_2O$, and esters which crystallise in needles. The alkyl acids are not altered by boiling with acetic acid, being unable to form a double lactone corresponding with *biscoumarin*.
C. H. D.

Digitogenic Acid and its Decomposition Products. HEINRICH KILIANI and J. SCHWEISSINGER (*Ber.*, 1904, 37, 1215—1221).—Digitogenic acid, prepared by Kiliani and Merk's method (*Abstr.*, 1902, i, 46), melts at 210° , whereas when prepared by the older method it melts at 155° ; it is shown that this is due to glacial acetic acid being used as the solvent, as this converts the substance melting at 155° into the less fusible form. The two modifications give the same analytical results, and apparently the same magnesium salt; by boiling the form melting at 210° with alcohol, it is partially reconverted into that melting at 155° .

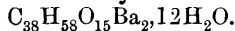
Digitic acid may be prepared by oxidising either of these modifications of digitogenic acid with alkaline potassium permanganate solution; details are given of its preparation and of that of its acid potassium salt, which is sparingly soluble in water, crystallises from 50 per cent. alcohol in nacreous leaflets, and melts at 235° . Analyses of the salt agree with either of the formulæ



or $C_{38}H_{61}O_{15}K$. The first explains the fact that when the salt is dissolved in boiling water, slender needles, apparently of digitic acid ($C_{20}H_{32}O_8$?), separate; on the other hand, barium digitate (Kiliani, *Abstr.*, 1891, 577), which was formerly considered to be



gives numbers agreeing more closely with the formula



Anhydrodigitic acid (Kiliani and Baylen, *Abstr.*, 1895, i, 65), on

titration with phenolphthalein as indicator, gives an equivalent 241. This does not agree with the previous formula, $C_{20}H_{28}O_6$, and analyses of the purified calcium salt are equally discordant. It appears that anhydridigitic acid is probably a mixture of acids; when it is fractionally precipitated from acetone by adding water, the less soluble material *A* gives, with magnesium nitrate in aqueous solution, an insoluble salt, whereas the more soluble acid *B* is not so precipitated. The fraction *A* has a mol. wt. 475, and fraction *B* a mol. wt. 489.

W. A. D.

p-Halogen-*o*-nitrobenzaldehydes. FRANZ SACHS (D.R.-P., 149748 and 149749).—*o*-Nitro-*p*-aminobenzaldoxime (Abstr., 1902, i, 377) is readily converted into *p*-halogen-*o*-nitrobenzaldehyde by boiling with haloid acids and a ferric salt. The hydroxylamine at first formed is probably oxidised by the ferric salt to nitrous acid, which then diazotises the amino-group. The oxime may also be converted into halogen derivatives by diazotising and boiling with a haloid acid and a cuprous salt.

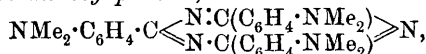
p-Chloro-*o*-nitrobenzaldehyde phenylhydrazone melts at 176—177° and the semicarbazone at 269—270°. *p*-Bromo-*o*-nitrobenzaldehyde, $C_7H_4O_3NBr$, melts at 97—98° and its phenylhydrazone at 181—182°. *p*-Iodo-*o*-nitrobenzaldehyde melts at 110—111° and its phenylhydrazone at 185°.

C. H. D.

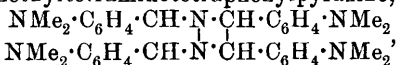
p-Dimethylaminobenzaldehyde. II. FRANZ SACHS and PAUL STEINERT (*Ber.*, 1904, 37, 1733—1745. Compare Abstr., 1903, i, 37).—*p*-Dimethylaminobenzaldehyde can be purified by distillation at 176—177° under 17 mm. pressure.

Hexamethyltriaminohydrobenzamide, $N_2(CH \cdot C_6H_4 \cdot NMe_2)_3$, formed by the action of alcoholic ammonia on dimethylaminobenzaldehyde, crystallises in colourless prisms, melts at 193°, is easily soluble in chloroform, less so in alcohol, and is insoluble in ether or light petroleum. In glacial acetic acid or acetic anhydride, it dissolves to a dark green solution, which becomes bluish-green on warming. The hydrochloride, $C_{27}H_{33}N_5 \cdot 3HCl$, melts at 264—265°; the picrate, $C_{27}H_{33}N_5 \cdot C_6H_3O_7N_3$, assumes a green colour at 160—170°, and melts at 213°; the oxalate melts at about 140—145°. When heated for 6 hours at 150—160°, hexamethyltriaminohydrobenzamide forms hexamethyltriaminocycaphenine and octomethyltetraminotetraphenylpyrazine.

Hexamethyltriaminocycaphenine,



forms trimetric crystals, melts at 357° (corr.), and is insoluble in acetone. Octomethyltetraminotetraphenylpyrazine,



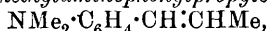
is precipitated from its alcoholic solution by aqueous ammonia as a voluminous yellow precipitate, melts at 95°, is soluble in acetone, and with bromine in alcoholic solution yields octomethyltetraminotetraphenyldibromopiperazine, which is dark red, melts at 95°, and loses its bromine when boiled with alcohol.

The *oxime* of *p*-dimethylaminobenzaldehyde melts at 144°. When boiled with acetic anhydride, it yields *p*-dimethylaminobenzonitrile, which boils without decomposition at 318° (corr.) under 758 mm. pressure and is volatile with steam.

p-Dimethylamino-*m*-nitrobenzamide, prepared by treating the nitrile with nitric and sulphuric acid, crystallises from water and melts at 210°.

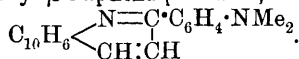
p-Nitrosomethylaminobenzonitrile, formed by the action of sodium nitrite and hydrochloric acid on *p*-dimethylaminobenzonitrile, has a yellow colour, crystallises from water, melts at 125°, and gives Liebermann's nitroso-reaction. When boiled with hydrochloric acid and stannous chloride, it yields *p*-methylaminobenzonitrile, which forms white crystals and melts at 85–86°.

With magnesium phenyl bromide, *p*-dimethylaminobenzaldehyde forms *p*-dimethylaminodiphenylcarbinol; with magnesium ethyl bromide, it forms *p*-dimethylaminophenylpropylene,



which melts at 48°.

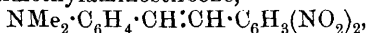
The action of *p*-dimethylaminobenzaldehyde on pyruvic acid and β -naphthylamine leads to the formation of 3-*p*-dimethylaminophenyl- β -naphthacinchonic acid, $\text{C}_{10}\text{H}_6 \begin{smallmatrix} \text{N} \\ \text{C}(\text{CO}_2\text{H}) : \text{CH} \end{smallmatrix} \text{C}_6\text{H}_4 \cdot \text{NMe}_2$, which melts at 293–295°, and at 300–310° loses carbon dioxide, yielding 3-*p*-dimethylaminophenyl- β -naphthaquinoline,



This crystallises in brown needles, melts at 245°, and is insoluble in most solvents. Dinitro-3-*p*-dimethylaminophenyl- β -naphthacinchonic acid, formed by nitration of the acid, melts at 260–263°.

p-Dimethylaminobenzylideneacetylacetone, prepared by acting with the aldehyde on acetylacetone in presence of piperidine, crystallises in yellow needles and melts at 95°. *p*-Dimethylaminobenzylidenebenzoylacetone, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CAc} \cdot \text{COPh}$, crystallises in yellow, monoclinic prisms, melts at 184°, dissolves in concentrated sulphuric acid to a yellow solution, and dyes wool yellow in acetic acid solution.

2' : 4'-Dinitro-4-dimethylaminostilbene,



obtained from *p*-dimethylaminobenzaldehyde and 2 : 4-dinitrotoluene, crystallises in long needles, melts at 181°, dissolves in concentrated sulphuric acid to a yellow and in glacial acetic acid to a dark red solution; in acetic acid solution it dyes wool reddish-brown. 2 : 6-Dinitrotoluene and *p*-dimethylaminobenzaldehyde form a *condensation product*. 2 : 4 : 6-Trinitrotoluene and *p*-dimethylaminobenzaldehyde form an *additive compound*, $\text{C}_9\text{H}_{11}\text{ON} \cdot \text{C}_7\text{H}_5\text{O}_6\text{N}_3$, which melts at 60° and is decomposed by mineral acids. G. Y.

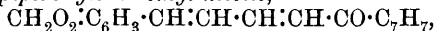
[Action of Formaldehyde and Lime on Cinnamaldehyde.]
BERNHARD TOLLENS (*Ber.*, 1904, 37, 1435. Compare Marle and Tollens, *Abstr.*, 1903, i, 493).—The products obtained by the action of formaldehyde and ammonium chloride are the *hydrochlorides* of bases

and not monomethylolacetophenone and trimethylolbisacetophenone. The *bases* are only slightly soluble in water and yield *platinichlorides*. The oil, previously described as phenyl vinyl ketone, is obtained when the hydrochlorides are distilled in steam, and is free from chlorine.

G. Y.

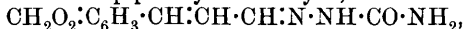
Condensations of Piperonylacraldehyde and of Piperonal. MAX SCHOLTZ and F. KIPKE (*Ber.*, 1904, 37, 1699—1704. Compare Abstr., 1895, i, 42, 464, 468).—With the three toluidines, piperonylacraldehyde forms an *o-toluidide*, which crystallises in long needles and melts at 94—95°, a *m-toluidide*, which crystallises in strongly refracting leaflets and melts at 95°, and a *p-toluidide*, which crystallises in leaflets and melts at 138°.

With acetylacetone, piperonylacraldehyde condenses in absolute alcoholic solution in presence of piperidine, with formation of *piperonyleneacetylacetone*, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}\text{Ac}_2$, which crystallises in yellow needles, melts at 105°, gives a deep violet coloration with concentrated sulphuric acid, and forms a *phenylhydrazone*; this crystallises in yellow needles and melts at 160—161°. In presence of an alkali, piperonylacraldehyde condenses with *p*-tolyl methyl ketone to form *p-tolyl piperonylenemethyl ketone*,



which crystallises in yellow needles, melts at 122°, and gives a deep violet coloration with concentrated sulphuric acid.

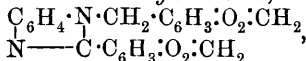
The *semicarbazone* of piperonylacraldehyde,



crystallises from pyridine in colourless leaflets and melts at 226°. At 227—230°, it is converted into 1-carbamido-5-piperonyl-4:5-pyrazoline (compare Scholtz, Abstr., 1896, i, 343; Harries, Abstr., 1899, i, 637), which forms a *picrate* and a hydrochloride. The *uranium tetrachloride* double salt, $\text{C}_{11}\text{H}_{11}\text{O}_3\text{N}_3(\text{UCl}_4)_2$, was the only pure product obtained. The *oxime* of piperonyleneacetone melts at 176°. At high temperatures, it loses water and yields a small amount of a *base*, which crystallises in leaflets and forms a *mercurichloride* melting at 186°.

Piperonal condenses with naphthyl methyl ketone less easily than with *p*-tolyl methyl ketone. The *product* forms yellow, granular crystals and melts at 141°. The condensation *product*, $\text{C}_{18}\text{H}_{13}\text{O}_2\text{N}$, of piperonal and β -naphthylamine crystallises from alcohol in leaflets containing 1 mol. $\text{C}_2\text{H}_6\text{O}$, and melts at 115°.

The action of piperonal on *o*-phenylenediamine, in alcoholic solution leads to the formation of the *aldehydine base*,

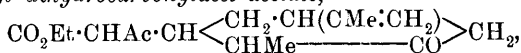


which forms yellow, granular crystals containing 1 mol. $\text{C}_2\text{H}_6\text{O}$, melts at 115—116°, and forms a *hydrochloride* melting at 277°.

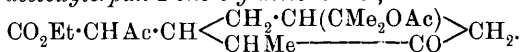
Ethyl piperonylacetacetate, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{C}\text{Ac}\cdot\text{CO}_2\text{Et}$, formed by the action of piperonal on ethyl acetoacetate in presence of piperidine, melts at 83° and forms a *phenylhydrazone* which crystallises in yellow leaflets and melts at 135°.

G. Y.

Syntheses of Bridged Dicyclic Systems. II. Addition of Ethyl Acetoacetate to Carvone. PAUL RABE and KARL WEILINGER (*Ber.*, 1904, 37, 1667—1671. Compare Abstr., 1903, i, 268, 269).—Ethyl chlorotetrahydrocarvonylacetoacetate reacts with zinc dust, glacial acetic acid, and concentrated hydrochloric acid yielding a mixture of *ethyl dihydrocarvonylacetoacetate*,

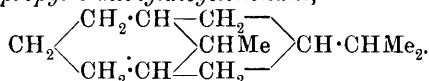


and *ethyl 8-acetoxyterpan-2-one-6-ylacetoacetate*,



The acetate crystallises from alcohol in six-sided, prismatic needles melting at 133°. It is the ketonic form, and by means of the sodium-derivative may be converted into the enolic form, which gives a purple coloration with ferric chloride.

The dihydro-ester is a colourless oil, gives a reddish-violet coloration with alcoholic ferric chloride, and readily decolorises alkaline permanganate. On reduction with sodium and alcohol, it yields *isopropenylmethyl-dicyclononanone* in the form of an oil distilling at 175—185° under 15 mm. pressure, and on further reduction yields the solid glycol melting at 172—173° (Abstr., 1903, i, 268). Both liquid and solid glycols, on reduction with phosphorus and hydriodic acid, yield *3-isopropyl-9-methyl-dicyclononane*,



It is a colourless liquid, which distils at 132° under 28 mm. pressure, or at 232—233° under 755 mm., has a sp. gr. 0.8643 at 20°/4°, n_D 1.4660 at 20°, and is optically inactive. J. J. S.

Syntheses of Bridged Dicyclic Systems. III. Addition of Ethyl Acetoacetate to Methylcyclohexenone. PAUL RABE (*Ber.*, 1904, 37, 1671—1674. Compare Abstr., 1903, i, 268, and preceding abstract).—3-Methylcyclo- Δ^2 -hexen-1-one (Hagemann, Abstr., 1893, i, 393; Knoevenagel, *ibid.*, 1895, i, 51) is obtained when ethyl methylcyclohexanoldicarboxylic acid (*Annalen*, 1904, 332, 1) is boiled with 10 per cent. sulphuric acid neutralised with ammonia and saturated with ammonium sulphate. The ketone is miscible with water in all proportions and condenses with ethyl acetoacetate in the presence of sodium ethoxide solution, yielding *methyl dicyclononanone*, $\text{CO}\begin{array}{c} \text{CH}_2\text{---CMe---CH}_2 \\ \text{CH}_2\cdot\text{C(OH)---CH}_2 \end{array} \text{CH}_2$, as a thick, yellow oil,

which distils at 170—173° under 17—18 mm. pressure, and on cooling partially solidifies. The *acetate* is an oil distilling at 172—176° under 16 mm. pressure. On reduction with sodium and alcohol, the ketoalcohol yields *1-methyl-dicyclononane-5:7-diol*, which crystallises from ether in colourless plates melting at 124—125°, and yielding a *diacetate* in the form of a thick oil. *1-Methyl-dicyclononane*, obtained by reducing the glycol with phosphorus and hydriodic acid, is a colourless liquid distilling

at 176—178° under 751 mm. pressure; it has a sp. gr. 0·8416 at 20°/4° and n_D 1·4529 at 20°. J. J. S.

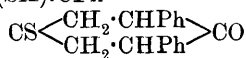
Preparation of Dibenzyl Ketone. HERMANN APITZSCH (*Ber.*, 1904, 37, 1428—1429. Compare Stobbe, *Annalen*, 1899, 308, 175; Young, *Trans.*, 1891, 59, 625; H. Wieland, this vol., i, 432).—Calcium phenylacetate is dried for an hour in flat porcelain dishes at 150—160°. The roughly powdered salt is heated in a non-tubulated retort of Jena glass over a Teclu burner. The distillate is dissolved in ether, dried with sodium sulphate, and fractionated. The yield of ketone, boiling at 324—325° under 739 mm. pressure, is 83 per cent. J. J. S.

Action of Carbon Disulphide and Potassium Hydroxide on Dibenzyl Ketone. HERMANN APITZSCH [and F. METZGER] (*Ber.*, 1904, 37, 1599—1610).—When dibenzyl ketone (preceding abstract) is boiled with carbon disulphide and solid potassium hydroxide, a compound insoluble in alkalis is obtained, and acids precipitate an orange compound of the formula $C_{18}H_{12}OS_3$, crystallising from chloroform in large, ruby-red crystals containing $CHCl_3$ and melting at 165°. It dissolves readily in ether, benzene, or ethyl acetate, and separates in each case with 1 mol. of solvent of crystallisation. The sodium derivative, $C_{18}H_{10}OS_3Na_2$, forms yellow, readily soluble needles containing $2C_2H_5\cdot OH$; the potassium (containing $12H_2O$), ammonium, and barium (with $10H_2O$) derivatives are described.

The diethyl ether, $C_{18}H_{10}OS_3Et_2$, forms characteristic, saw-blade like crystals and melts at 141·5—142°. The dibenzyl ether crystallises from benzene and melts at 131°. The dipropyl ether forms almost colourless, glistening crystals and melts at 88°; the dimethyl ether forms white crystals and melts at 167°. The ethers are only slowly hydrolysed by heating with alcoholic hydrogen chloride or potassium hydroxide at 300°. The dibenzoyl ester forms yellow needles and melts at 142°.

Solutions of the acid compound in indifferent solvents decompose on exposure to light, forming a crystalline complex anhydride. Zinc and hydrochloric acid remove 2 atoms of sulphur from the acid compound, forming a compound, $C_{18}H_{16}OS$, crystallising from alcohol in colourless needles melting at 136·5° and having no acid properties.

The orange acid compound is probably 1-keto-2:6-diphenyl-4-thiophen-3:5-dithiol, $CS \begin{smallmatrix} \text{C}(\text{SH})\cdot\text{CPh} \\ \text{C}(\text{SH})\cdot\text{CPh} \end{smallmatrix} \text{CO}$, yielding



on reduction.

Diethyl ketone yields a similar orange compound, which will be further investigated. C. H. D.

Reduction of Ketones. H. APITZSCH and F. METZGER (*Ber.*, 1904, 37, 1676—1679).—A theoretical yield of hydrobenzoin (m. p. 134°) may be obtained by the reduction of benzoin with stannous chloride in the presence of alcoholic hydrogen chloride. Anisoin, when reduced in a similar manner, yields isohydroanisoin

melting at 109°, but cuminoïn cannot be reduced by a similar process. Methyl- and ethyl-benzoin (Fischer, Abstr., 1894, i, 38) and benzoin-anilide are not reduced even in sealed tubes at 120°, but at 140° they are decomposed yielding benzoin, which is then reduced.

Benzil with an excess of stannous chloride is quantitatively reduced to hydrobenzoin, and anisil to *isohydroanisoin*.

Acetophenone, benzophenone, deoxybenzoin, dibenzyl ketone, benzylacetophenone, and benzylideneacetophenone could not be reduced. Acetone yields methyl and *isopropyl* alcohols and mesityl oxide. Benzoquinone and phenanthraquinone are reduced to the corresponding quinols, but anthraquinone is not affected. J. J. S.

Decomposition of Methiodides in Acid Solution. PAUL RABE and WILLIAM DENHAM (*Ber.*, 1904, 37, 1674—1675).—When cinchonine methiodide is warmed in dilute acetic acid solution for 72 hours, the ring is ruptured and methylcinchotoxin is formed (Claus and Müller, Abstr., 1880, 289; 1895, i, 435). The reaction is similar to the rupture of bridged rings previously observed in alkaline solution (Claus and Müller, *loc. cit.*; Freund and Rosenstein, *ibid.*, 1894, i, 151). J. J. S.

Desmotropism of Halogen-substituted Acid Methylene Groups in the Diketohydrindene Series. LEOPOLD FLATOW (*Ber.*, 1904, 37, 1787—1790).—A theoretical discussion of the facts already published by the author (Abstr., 1901, i, 543). It is shown that in the diketohydrindene series the compound obtained by replacing hydrogen by bromine has enolic characteristics, whereas on replacing hydrogen by chlorine a compound is obtained which reacts as a ketone. E. F. A.

Quinonedimide. RICHARD WILLSTÄTTER and EUGEN MAYER (*Ber.*, 1904, 37, 1494—1507).—*Quinonedimide dihydrochloride*, obtained by the action of hydrogen chloride on quinone dichloroimide, rapidly decomposes in moist air; the salt is slightly yellow, dissolves in much water without coloration, but with small quantities of water it gives green, brown, and finally violet shades. A similar behaviour is shown by the solutions in fairly concentrated mineral acids. To obtain *quinonedimide* from this salt, ammonia gas is passed into the ethereal suspension of the compound, but special precautions are necessary for success to be obtained. The pure diimide forms bright yellow, monoclinic prisms, which, on warming, decompose between 50° and 60°. It explodes on heating on the water-bath, violently when concentrated sulphuric acid is added. It yields *p*-phenylenediamine on reduction; when warmed with dilute mineral acids, quinone and ammonia are formed. The aqueous solution rapidly decomposes forming a product, which behaves similarly to Bandrowski's tetra-aminodiphenyl-*p*-azophenylene (Abstr., 1894, i, 236), which the authors find can be crystallised from nitrobenzene and aniline, and then forms green crystals with a metallic lustre, melting at 238°. E. F. A.

Oxidation Product from *p*-Tolylenediamine. JULIUS SCHMIDT and ADOLF SAAGER (*Ber.*, 1904, 37, 1679—1680. Compare Willstätter and Mayer, preceding abstract).—A *toluquinonemonoimide hydrochloride*, $O:C_6H_3Me:NH, HCl$ [$O:Me:NH = 1:2:4$ or $1:3:4$], may be obtained by oxidising a 1 per cent. aqueous solution of *p*-tolylene-diamine hydrochloride with ferric chloride at the ordinary temperature and then saturating with common salt. It crystallises from hot dilute hydrochloric acid in small, purple-black needles, and its solutions in water or alcohol are blue, but are decolorised by the addition of alkalis. J. J. S.

Preparation of Amino- and Hydroxy-anthraquinones and their Halogen Derivatives. BASLER CHEMISCHE FABRIK (D.R.-P. 148110).—Heating with sulphuric acid converts amino- and hydroxy-benzoyl-*o*-benzoic acids (prepared by nitration and reduction of benzoyl-*o*-benzoic acid) almost quantitatively into amino- or hydroxy-anthraquinones. The same reaction occurs with the halogen-substituted *m*-amino- and *m*-hydroxy-benzoyl-*o*-benzoic acids, which may be prepared either by condensing halogenated phthalic anhydrides with benzene or its halogen derivatives, nitrating, and reducing; or by condensing phthalic anhydride with halogenated benzenes, nitrating, and reducing.

m-Nitrobenzoyl-*o*-benzoic acid crystallises from acetic acid and melts at 186—187°. Iron and hydrochloric acid reduce it to *m*-aminobenzoyl-*o*-benzoic acid, melting and decomposing at 165°. The diazo-compound of the latter substance, when boiled, yields *m*-hydroxybenzoyl-*o*-benzoic acid, which melts at 181—182°. Heating with sulphuric acid converts these acids into mixtures of α - and β -amino- or hydroxy-anthraquinones.

p-Chloro-*m*-nitrobenzoyl-*o*-benzoic acid, prepared by nitrating *p*-chlorobenzoyl-*o*-benzoic acid, crystallises from alcohol and melts at 202—204°, and on reduction yields *p*-chloro-*m*-aminobenzoyl-*o*-benzoic acid, melting at 175—176°. Heating with sulphuric acid converts the amino-acid into 3-chloro-2-aminoanthraquinone, melting at 280—283°. 3-Chloro-2-hydroxyanthraquinone forms golden-yellow needles and melts at 258—260°. 3-Bromo-2-aminoanthraquinone melts at 267—270°, and 3-bromo-2-hydroxyanthraquinone at 249—252°.

C. H. D.

[1-Amino-5- and -8-hydroxyanthraquinones.] FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 149780).—1-Amino-5- and -8-hydroxyanthraquinones are conveniently prepared by nitrating anthraquinone-*a*-sulphonic acid, separating the 1:5- and 1:8-nitroanthraquinonesulphonic acids, reducing, and heating with lime under pressure (compare Wacker, *Abstr.*, 1903, i, 132). Brown- or orange-coloured monobromo-derivatives are obtained by suspending the amino-hydroxyanthraquinones in water, warming to 60°, adding bromine slowly, and heating to 100°. They dissolve sparingly in organic solvents. The condensation product from *p*-toluidine crystallises from pyridine or chlorobenzene in dark blue needles and dissolves in aniline to a greenish-blue solution. C. H. D.

4-Nitroalizarin 2-Alkyl Ethers. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 150322).—Whereas on nitration alizarin yields a mixture of nitroalizarins with nitropurpurin and purpurin, the alkyl ethers readily form well-defined nitro-compounds, the nitro-group occupying the 4-position.

4-Nitroalizarin 2-methyl ether, $C_6H_4 \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} C_6H(OH)(NO_2) \cdot OMe$, prepared by nitrating alizarin 2-methyl ether, crystallises from glacial acetic acid in yellow leaflets, melts at $280-282^\circ$ (uncorr.), and dissolves sparingly in alcohol, ether, or benzene, readily in nitrobenzene. The alkali salts form red needles. **4-Aminoalizarin 2-methyl ether** forms a reddish-brown powder, dissolving with difficulty in hot dilute solutions of alkali hydroxides. The solution in concentrated sulphuric acid shows a yellow fluorescence on the addition of boric acid.

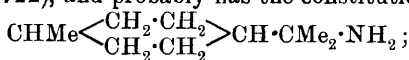
The *ethyl ether* closely resembles the methyl compound.

C. H. D.

Preparation of Anthraquinone- α -sulphonic Acid. FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 149801).—Anthraquinone- α -sulphonic acid is obtained in a pure state, free from β -acid or disulphonic acids, when anthraquinone is sulphonated in the presence of small quantities of mercury or mercury salts. The *potassium salt* crystallises in bright yellow, glistening leaflets, sparingly soluble in water; when heated at $180-190^\circ$ with aqueous ammonia, it yields the characteristic α -aminoanthraquinone.

C. H. D.

Nitro-compounds of the Menthane Series. II. MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 237—246. Compare Abstr., 1900, i, 324).—Menthane is readily nitrated by nitric acid of sp. gr. 1.075 both in open and closed vessels, the main product in either case being *tert.-nitromenthane*, $C_{10}H_{19} \cdot NO_2$, which is a colourless, mobile liquid boiling at $135-137^\circ$ under 25 mm. pressure, has the sp. gr. 1.0005 at $0^\circ/0^\circ$ and 0.9871 at $22^\circ/0^\circ$ and n_D 1.46241 at 22° . On reduction by means of tin and hydrochloric acid, it yields a *menthylamine*, $C_{10}H_{19} \cdot NH_2$, which boils at $199-200^\circ$ under 750 mm. pressure and has the sp. gr. 0.8690 at $0^\circ/0^\circ$ and 0.8451 at $22^\circ/0^\circ$ and n_D 1.45622 at 22° . This compound is not identical with either the menthylamine or the carvomenthylamine previously described by Baeyer (Abstr., 1893, i, 722), and probably has the constitution



the *hydrochloride* melts at $140-150^\circ$ and the *platinichloride* decomposes at 220° ; the *benzoyl* derivative separates from light petroleum in stellate aggregates of crystals melting at 153° ; the *nitrate* and *sulphate* are readily soluble in water, and the *oxalate* only slightly so.

The *benzoyl* derivative of *menthonamine*, $C_{17}H_{23}O_2N$, separates from light petroleum in white needles, which melt at $145-146^\circ$ and dissolve readily in benzene, in which solvent it has $[\alpha]_D - 30.48^\circ$. T. H. P.

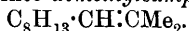
Farnesol, a New Sesquiterpene Alcohol. HAARMANN & REIMER (D.R.-P. 149603).—The only sesquiterpene alcohol hitherto

known has been santalol (von Soden, Abstr., 1900, i, 677). *Farnesol*, $C_{15}H_{26}O$, a new sesquiterpene alcohol, is obtained from various acacia oils, from musk oil, and from lime-tree blossom oil, by saponifying the esters present, distilling under 200 mm. pressure, and converting the fraction boiling at $150-200^\circ$ into esters by means of phthalic or other anhydride. Farnesol is a colourless oil with a fragrant odour, boiling at 160° (uncorr.) under 10 mm. pressure; it has a sp. gr. 0.885 and n_D 1.488. C. H. D.

Mechanism of the Dehydration of Menthol by Organic Acids. I. ZELIKOW (*Ber.*, 1904, 37, 1374-1383).—See Abstr., 1903, i, 184. C. H. D.

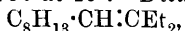
Campholene Derivatives. AUGUSTE BÉHAL (*Bull. Soc. chim.*, 1904, 31, 461-466. Compare Abstr., 1902, i, 419, and this vol., i, 329).—*Dimethylcamphenol*, $\begin{matrix} CMe_2 \cdot CMe \\ | \\ CH_2 - CH_2 \end{matrix} > C \cdot CH_2 \cdot CMe_2 \cdot OH$, prepared by the action of magnesium methyl iodide on methyl camphenolate, boils at $110-112^\circ$ under 23 mm. and at $218-220^\circ$ under the atmospheric pressure, has a sp. gr. 0.9116 at 0° and 0.8996 at 16° , and n_D 1.4722 at 16° . The *acetyl* derivative, obtained by the action of acetic anhydride on the magnesium bromide derivative of the alcohol, boils at $118-122^\circ$ under 19 mm. pressure, has a sp. gr. 0.9387 at 0° and 0.9266 at 16° , and n_D 1.46459.

When dimethylcamphenol is slowly distilled with acetic anhydride, it is converted principally into *dimethylcampholandiene*,

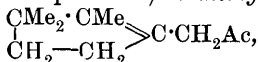


This boils at $188-190^\circ$, has sp. gr. 0.8421 at 0° and 0.8311 at 16° , and n_D 1.46707 at 16° . A mixture of this hydrocarbon with dimethylcampholene oxide is produced when dimethylcamphenol is heated with sulphuric acid.

Diethylcamphenol, prepared in an analogous manner, boils at $144-148^\circ$ under 28 mm. pressure, has a sp. gr. 0.9250 at 0° and 0.9113 at 19° , and n_D 1.47730 at 19° . *Diethylcampholandiene*,

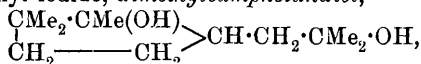


boils at $222-224^\circ$, has a sp. gr. 0.8814 at 0° and 0.8688 at 19° , and n_D 1.46875 at 19° , whence the molecular refraction is 61.4, whereas that calculated from the formula adopted is 63.64. This difference seems to imply the presence of a second closed chain, in which case the calculated molecular refraction would be 61.94. *Diethylcampholenyl acetate* is liquid, and decomposes even when heated under 14 mm. pressure. When campholenonitrile is treated with magnesium methyl iodide, a small yield (5 to 6 per cent.) of *methylcamphenone*,

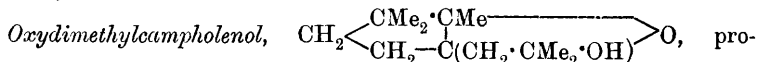


is obtained; this boils at $210-212^\circ$, has a sp. gr. 0.9343 at 0° and 0.9247 at 15° , and n_D 1.47172 at 15° . *Ethylcamphenone*, similarly prepared, boils at $222-225^\circ$, has sp. gr. 0.9322 at 0° and 0.9210 at

16°, and n_D 1.46796 at 16°. When campholenolactone is treated with magnesium methyl iodide, *dimethylcampholandi*ol,



is formed; this melts at 92—94°, and is soluble in benzene and hot alcohol.



duced by the interaction of magnesium methyl iodide with ethyl ketocampholenate and decomposition of the magnesium compound first formed with water and sulphuric acid, crystallises from alcohol and melts at 142°. T. A. H.

Transformation Products of Pulegonehydroxylamine. CARL D. HARRIES and LOUIS ROY (*Ber.*, 1904, 37, 1341. Compare *Abstr.*, 1898, i, 573, and Semmler, this vol., i, 437).—When pulegone is boiled with a solution of hydroxylamine hydrochloride in water, no pulegonehydroxylamine is produced, but an oily, basic compound. The same compound may be prepared by warming pulegonehydroxylamine with 20 per cent. hydrochloric acid on the water-bath, and is precipitated by potassium hydroxide as a yellow, viscous oil, which boils at 102—106° under 13 mm. pressure. It is derived from pulegonehydroxylamine by the loss of water, $\text{C}_{10}\text{H}_{19}\text{O}_2\text{N} - \text{H}_2\text{O} = \text{C}_{10}\text{H}_{17}\text{ON}$, and forms an oxalate and picrate. Its properties are under investigation.

C. H. D.

Derivatives of Thujone. LEO TSCHUGAEFF (*Ber.*, 1904, 37, 1481—1486. Compare Semmler, this vol., i, 438; Kondakoff and Skworzoff, *ibid.*, 439).—The relationship of the formulæ proposed for α - and β -thujenes to those for α -tanacetonedicarboxylic acid and homotanacetonedicarboxylic acid, put forward by Semmler, is pointed out. *Thujamenthene*, $\text{C}_{10}\text{H}_{18}$, prepared by carefully decomposing the compound, $\text{C}_{10}\text{H}_{19} \cdot \text{O} \cdot \text{CS} \cdot \text{SCH}_3$, formed from thujamenthol, boils at 157—159° and has a sp. gr. 0.8046 at 20°/4° and n_D 1.44591 at 20°; it forms a crystalline nitrosochloride.

E. F. A.

Essential Oils obtained by Extracting Fresh Flowers with Volatile Solvents (Essential Flower-extract Oils). HUGO von SODEN (*J. pr. Chem.*, 1904, 69, 256—272).—These flower-extracts are obtained by extracting the fresh flowers in the cold with light petroleum and distilling off the solvent; they were freed from wax, colouring matters, &c., by solution in cold alcohol, and were finally distilled with steam, the distillate being extracted with ether.

Violets.—Yield of the purified oil: 0.003 per cent. of the fresh flowers; colour, pale greenish-yellow; sp. gr. 0.920 at 15°; rotation, +104°15' (in 100 mm. tube?); acid number, 10; ester number, 37.

Orange flowers.—Yield: 0.06 per cent. Sp. gr. 0.9245 at 15°; rotation, -2°30' in 100 mm. tube; acid number, 4; ester number, 102 (corresponding with 35.7 per cent. linalyl acetate); methyl anthranilate, 6.9 per cent. (leaving 26.7 per cent. linalyl acetate).

Reseda.—Yield: 0.003 per cent; colour, yellow; sp. gr. 0.961 at 15°; rotation, +31°20' at 17° in 100 mm. tube; acid number, 16; ester number, 85; solidifies when cooled.

Roses.—*French*: Yield: 0.52 per cent.; colour, reddish-yellow; sp. gr. 0.967 at 15°; rotation, -1.55° at 17° in 100 mm. tube; acid number, 5.5; ester number, 4.6 (corresponding with 1.6 per cent. of geranyl acetate); acetyl number, 295; solidifies at 7—5°. Contains phenylethyl alcohols, 60; aliphatic terpene alcohols (geraniol, nerol, citronellol), 20 per cent. *German*: Yield: 1.07 per cent.; colour, golden-yellow; sp. gr. 0.984 at 19°; rotation, +0°9' at 17°; acid number, 3; ester number, 4 (corresponding with 1.40 per cent. of geranyl acetate); acetyl number, 313.5; solidifies at 18—12°. Contains phenylethyl alcohol, 75; primary aliphatic terpene alcohols, 15 per cent.

Jasmine (2 samples).—Yield: 0.077, 0.072 per cent.; colour, reddish-yellow; sp. gr. 0.9955, 0.967, at 15°; rotation, -1°, feebly, in 100 mm. tube; acid number, 2.5, 3.5; ester number, 190, 161.5 (corresponding with 51, 43.3, per cent. of benzyl acetate). Contains indole.

Cassia.—Yield: 0.084 per cent.; colour, reddish-yellow; sp. gr. 1.047 at 27°; rotation, -0°40' at 25° in 100 mm. tube; acid number, 42.5 (corresponding with 10.3 per cent. of salicylic acid); ester number, 114 (corresponding with 30.9 per cent. of methyl salicylate); solidifies at 21—18°. C. F. B.

Oil of Jasmine Blossoms. VII. ALBERT HESSE (*Ber.*, 1904, 37, 1457—1463. See Abstr., 1901, i, 732).—In two experiments, the extract, obtained by treatment of fresh jasmine blossoms, gave no reaction for methyl anthranilate until after distillation in steam, when the ethereal oil (yield, 0.0447 and 0.0442 per cent.) was found to contain 0.42—0.377 per cent. of methyl anthranilate and 2.1—2.0 per cent. of indole.

An ethereal extract of fresh blossoms gave no reaction for methyl anthranilate either before or after distillation in steam. The ethereal oil gave no reaction for indole. The author considers that the anthranilate and the indole are present in the fresh blossoms as compounds which are easily decomposed by distillation, by the process of "enfleurage," and even by extraction under certain conditions.

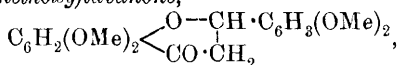
G. Y.

Two New Algerian Essential Oils. PAUL JEANCARD and C. SATIE (*Bull. Soc. chim.*, 1904, 31, 478—480).—Scheih oil is reddish-brown, with an odour resembling that of absinthe, and is soluble in its own volume of alcohol (80°). It has a sp. gr. 0.9540 at 9.5°, specific viscosity 170 seconds at 9.5°, acid number 8.4, and saponification values 66.5 and 129.5 respectively before and after acetylation. It contains 15 per cent. of phenolic substances, of which pyrogallol dimethyl ether was isolated. The oil, after removal of phenols, gave on fractional distillation 15 per cent. below 190°, 17.4 per cent. between 190° and 200°, and 48 per cent. above 200°. The two latter fractions probably contain respectively thujone and thujol.

Gouft oil is bright yellow and possesses a terpenoid odour; it has a sp. gr. 0.8720 at 9.5°, acidity 1.12, and saponification values 14 and 42 respectively before and after acetylation: 4.6 per cent. of the oil distils below 155°, the same proportion between 155° and 160°, 44.4 per cent. from 160° to 165° and 13 per cent. from 165° to 170°. The third fraction contains *l*-pinene and the last a primary alcohol with a geraniol-like odour.

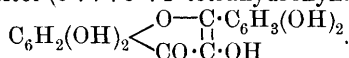
T. A. H.

Synthesis of Quercitol. STANISLAUS VON KOSTANECKI, VICTOR LAMPE, and JOSEF TAMBOR (*Ber.*, 1904, 37, 1402—1405).—Kostanecki and Tambor's 2'-hydroxy-4':6':3:4-tetramethoxychalkone (this vol., i, 426), when boiled with dilute hydrochloric acid and alcohol, yields 5:7:3':4'-tetramethoxyflavanone,



which crystallises from carbon disulphide in colourless, thick needles, melting at 159—160°, and soluble in sodium hydroxide solution. Amyl nitrite and concentrated hydrochloric acid convert this into an isonitroso-derivative, $\text{C}_6\text{H}_2(\text{OMe})_2 \begin{array}{l} \text{O} - \text{CH} \cdot \text{C}_6\text{H}_3(\text{OMe})_2 \\ \text{CO} \cdot \text{C} \cdot \text{N} \cdot \text{OH} \end{array}$, which crystal-

lises from benzene in small, almost colourless needles melting and decomposing at 183°, and soluble in alkali and in concentrated sulphuric acid. When dissolved in acetic acid and boiled with 10 per cent. sulphuric acid, the isonitroso compound yields hydroxylamine and 5:7:3':4'-tetramethoxyflavonol, which crystallises in yellow needles melting at 197—198°. This does not dissolve in cold alkalis, and, with warm sodium hydroxide, it yields a sparingly soluble, yellow sodium derivative. It dyes alumina and iron mordants to a certain extent, and, when boiled for some time with concentrated hydriodic acid, yields quercitol (5:7:3':4'-tetrahydroxyflavonol),



When purified by aid of its acetyl derivative and crystallised from dilute alcohol, it forms lemon-yellow, glistening needles melting and decomposing at 313—314°. Its *penta-acetyl* derivative melts at 193—194°.

J. J. S.

Reactivity of Substituted Phloroglucinols in the Formation of Fluorones. A. SCHREIER and FRANZ WENZEL (*Monatsh.*, 1904, 25, 311—318. Compare *Abstr.*, 1900, i, 308).—When warmed together with hydrochloric acid, methylphloroglucinolcarboxylic acid and salicylaldehyde react easily with evolution of carbon dioxide. On cooling, the reaction mixture solidifies to a mass of delicate, red needles, which consist of a mixture of the hydrochlorides of 8-hydroxy-5-(or 7-)-methylfluorone and of 8-hydroxy-5-(or 7-)-methylfluoronecarboxylic acid. On boiling with concentrated hydrochloric acid, the carboxylic group is completely eliminated, and, on cooling, the hydrochloride of 8-hydroxymethylfluorone, $\text{C}_{14}\text{H}_{10}\text{O}_3 \cdot \text{HCl}$, separates in violet, metallic crystals.

The action of bromine in chloroform solution on methylphloro-

glucinolcarboxylic acid leads to the formation of dibromomethylphloroglucinol, which melts at 132—134° and is insoluble in aqueous potassium hydrogen carbonate, and *bromomethylphloroglucinolcarboxylic acid*, $C_8H_7O_5Br \cdot H_2O$, which crystallises in delicate, whiteneedles, melts at 149° or at 159—161° when anhydrous, and gives a blue coloration with ferric chloride. When boiled with water, it loses carbon dioxide and yields *bromomethylphloroglucinol*, $C_7H_7O_3Br \cdot 4H_2O$, which crystallises in long, transparent, yellow needles, melts at 129—130°, and loses $4H_2O$ when heated at 100°.

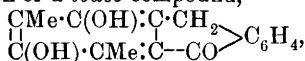
Bromomethylphloroglucinol and salicylaldehyde, when heated in acetic acid solution along with hydrochloric acid, enter into reaction, but, on cooling, there is no crystalline separation. On the addition of water, a red, amorphous *substance* is precipitated. This is soluble in alcohol, benzene, or chloroform, but cannot be obtained in the crystalline state.

The introduction of a bromine atom into methylphloroglucinol does not favour the fluorone formation, as does the presence of a carboxylic group. G. Y.

8-Hydroxy-5:7-dimethylfluorone. J. LIEBSCHÜTZ and FRANZ WENZEL (*Monatsh.*, 1904, 25, 319—331. See foregoing abstract).—Dimethylphloroglucinol methyl ether [$Me_2:OMe:(OH)_2 = 1:3:4:2:6$] (Bosse, Abstr., 1901, i, 207) and salicylaldehyde in acetic acid solution give an intense red coloration immediately on addition of concentrated hydrochloric acid. The product, *8-methoxy-5:7-dimethylfluorone* (?), is precipitated as a red, amorphous mass on addition of water. It is soluble in methyl or ethyl alcohol, ether, or benzene, and is precipitated from its solution in aqueous sodium hydroxide on addition of sulphuric acid. When warmed with concentrated hydrochloric acid, it yields 8-hydroxy-5:7-dimethylfluorone, from which it can be formed by the action of diazomethane.

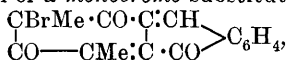
Under the same conditions, dimethylphloroglucinol methyl ether [$Me_2:OMe:(OH)_2 = 1:3:2:4:6$] (Abstr., 1902, i, 464) condenses with salicylaldehyde only on prolonged contact. The bluish-grey, amorphous *product*, which is precipitated on addition of water, does not yield hydroxydimethylfluorone. These facts confirm the constitution assigned to 8-hydroxy-5:7-dimethylfluorone.

Reduction of 8-hydroxy-5:7-dimethylfluorone with sodium amalgam leads to the formation of a *leuco*-compound,



which crystallises in colourless needles, melts at 185—186°, is oxidised easily on exposure to air, and forms a *diacetyl* derivative. This crystallises in yellow needles and melts at 117—118°.

The action of 1 mol. bromine on 8-hydroxy-5:7-dimethylfluorone leads to the formation of a *monobromo*-substitution product,



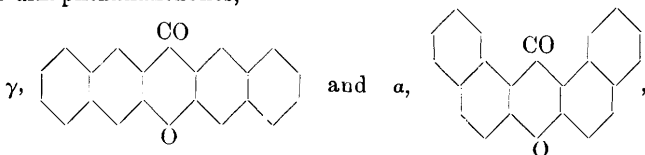
which crystallises in ruby-coloured prisms and decomposes at 170—180°.

With bromine, the monobromo-compound forms an *additive* compound, $\text{CBrMe} \cdot \text{CO} \cdot \text{CBr} \cdot \text{CHBr} > \text{C}_6\text{H}_4$ (?), which is obtained as an amorphous mass. With methyl alcohol, it evolves hydrogen bromide and yields

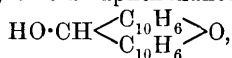
a *dibromomethoxy*-derivative, $\text{CBrMe} \cdot \text{CO} \cdot \text{CBr} \cdot \text{CH}(\text{OMe}) > \text{C}_6\text{H}_4$, which crystallises in yellow, transparent plates, melts at $117\text{--}118^\circ$, and becomes red when exposed to light. The *dibromoethoxy*-derivative, formed by the action of ethyl alcohol on the tribromo-compound, crystallises in yellow, hexagonal plates and melts at $102\text{--}104^\circ$.

G. Y.

The Dinaphthaxanthene Series. ROBERT FOSSE (*Compt. rend.*, 1904, 138, 1051—1054. Compare *Abstr.*, 1901, i, 604, 643; 1902, i, 171, 304, 368, 689; 1903, i, 49, 357; this vol., i, 82, 336, 337).—Of the dinaphthaxanthones,



the first (γ) was prepared by Kostanecki from $\beta\beta$ -naphtholcarboxylic acid and melts at 241° (*Abstr.*, 1892, 1099), whilst the second (α) was prepared by Bender from β -naphthyl ethyl carbonate (*Abstr.*, 1881, 48) and by Kostanecki from $\alpha\beta$ -hydroxynaphthoic acid, and can also be obtained by the action of an alkali carbonate on β -naphthyl carbonate according to the equation: $2\text{CO}(\text{OC}_{10}\text{H}_7)_2 = \text{CO}_2 + 2\text{C}_{10}\text{H}_7\text{OH} + \text{CO} < \text{C}_{10}\text{H}_6 > \text{O}$; it melts at 194° and, on reduction with nascent hydrogen, yields dinaphthaxanthhydrol,



m. p. 145° , from which dinaphthaxanthonium salts, $\text{CH} < \text{C}_{10}\text{H}_6 > \text{OX}$, are obtained by the action of hydracids, and dinaphthaxanthene, $\text{CH}_2 < \text{C}_{10}\text{H}_6 > \text{O}$, melting at 201° , by the action of acetic acid and alcohol.

A compound obtained by Bender by oxidising methyl dinaphthaxanthene, $\text{CHMe} < \text{C}_{10}\text{H}_6 > \text{O}$, melting at 149° , described as a third dinaphthaxanthone, has probably a different constitution, since it gives a reduction product melting at 165° . M. A. W.

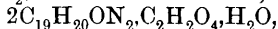
The Indophenine Reaction. FRANZ W. BAUER (*Ber.*, 1904, 37, 1244—1245. Compare Schwalbe, this vol., i, 337).—Thiophen, in benzene solution, fails to give the indophenine reaction with isatin when pure sulphuric acid is employed; if, however, a trace of ferric

chloride or nitric acid is added to the acid, the characteristic deep blue colour is at once produced.

W. A. D.

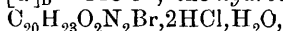
Bromine Derivatives of the Cinchona Alkaloids, and the Corresponding Compounds containing less Hydrogen. A. CHRISTENSEN (*J. pr. Chem.*, 1904, [ii], 69, 193—222. Compare Abstr., 1901, i, 481; 1904, i, 184).—Skalweit's dibromocinchonidine and dihydroxycinchonidine (Abstr., 1874, 808) must have been cinchonidine dibromide and dehydrocinchonidine respectively. Galimard's α - and β -dibromocinchonidines (Abstr., 1901, i, 162) were probably both cinchonidine dibromide.

Bromocinchonidine, $C_{19}H_{21}ON_2Br$, obtained by the action of cold alcoholic potassium hydroxide on cinchonidine dibromide, melts at 218° and has $[\alpha]_D - 110.3^\circ$ in 2 per cent. solution in a mixture of chloroform and alcohol (2 : 1 vols.); its *oxalate*, $2C_{19}H_{21}ON_2Br, C_2H_2O_4, 2H_2O$, and a *hydrobromide*, $C_{19}H_{21}ON_2Br, 2HBr, 2H_2O$, were analysed. Prolonged boiling with alcoholic potassium hydroxide converts it into *dehydrocinchonidine*, $C_{19}H_{20}ON_2$, which melts at 194° ; the *oxalate*,

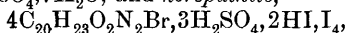


melting just above 190° , and *hydrochloride*, $C_{19}H_{20}ON_2, HCl, 2H_2O$, of this base were analysed. The base, when treated with hydrogen bromide and bromine in acetic acid solution, forms *dibromocinchonidine hydrobromide perbromide*, $C_{19}H_{20}ON_2Br_2, 2HBr, Br_2$; by treating this with sulphurous acid and precipitating with ammonia, *dibromocinchonidine*, $C_{19}H_{20}ON_2Br_2$, melting at 186° , is obtained.

Bromoquinine, $C_{20}H_{23}O_2N_2Br$, obtained from quinine dibromide, melts at 210° and has $[\alpha]_D - 118.1^\circ$; the *hydrochloride*,



hydrobromide, $C_{20}H_{23}O_2N_2Br, 2HBr, 3H_2O$ and anhydrous, *sulphate*, $2C_{20}H_{23}O_2N_2Br, H_2SO_4, 7H_2O$, and *herepathite*,



were analysed. *Dehydroquinine*, $C_{20}H_{22}O_2N_2$, was obtained in the crystalline state, although not without difficulty; it melts at 184° , has $[\alpha]_D - 178^\circ$ and -180° respectively in 1.42 and 2.85 per cent. solution in a mixture of chloroform and alcohol, and dissolves in water to the extent of 0.246 gram in 100 c.c. The *oxalate*, $2C_{20}H_{22}O_2N_2, C_2H_2O_4, xH_2O$, melting at 133 — 134° , *hydrochloride*, $C_{20}H_{22}O_2N_2, HCl, xH_2O$, and *herepathite*, $4C_{20}H_{22}O_2N_2, 3H_2SO_4, 2HI, I_4$, were analysed; the last was amorphous and not quite pure. Dehydroquinine appears to form a dibromo-additive product, presumably dibromoquinine, but this could not be obtained pure.

C. F. B.

Synthesis of Nicotine. AMÉ PICTET and ARNOLD ROTSCHY (*Ber.*, 1904, 37, 1225—1235).—The following results were necessary to render the synthesis of nicotine from 3-aminopyridine complete (compare Pictet and Crépieux, Abstr., 1895, i, 627; 1898, i, 688; Pictet, Abstr., 1900, i, 685). (1) The production of nicotyrine from its methiodide; (2) the identification of tetrahydronicotyrine with *i*-nicotine; (3) the resolution of *i*-nicotine into its optical antipodes and the identification of the *l*-form with the natural alkaloid. These have been successfully realised.

Attempts to remove methyl iodide from nicotyrine methiodide by

dry distillation were without issue, and on heating the methiodide with water for 3 hours at 200° a base was obtained which yielded a picrate melting at 120° , and was therefore obviously not identical with nicotine. The desired result was, however, obtained by distilling the methiodide with lime; it was identified by its boiling point, by its picrate, melting at 162° , and by its platinichloride.

Tetrahydronicotyrine was identified as *i*-nicotine (*loc. cit.*) by its boiling point, density, and by its giving the same platinichloride, $C_{10}H_{14}N_2, H_2PtCl_6, H_2O$; the *picrate* melts at 218° , the *dihydriodide* at 195° , and the *dimethiodide* at 219° . The resolution of the acid into its components was effected by means of the ditartrate, $C_{10}H_{14}N_2, 2C_4H_6O_6, 2H_2O$, which is best prepared in aqueous, not alcoholic, solution (compare Dreser, *Abstr.*, 1889, 730). *l*-Nicotine *d*-ditartrate has $[\alpha]_D + 27.16^{\circ}$ at 15° and $+26.60^{\circ}$ at 27° , calculated for the anhydrous salt; it melts at $88-89^{\circ}$ and is much less soluble than *d*-nicotine *d*-ditartrate, which can only be obtained as a syrup. *l*-Nicotine, prepared from the ditartrate, boils at $246-246.5^{\circ}$ under 734.5 mm. pressure, has a sp. gr. 1.0177 at $10^{\circ}/4^{\circ}$, 1.0092 at $20^{\circ}/4^{\circ}$, and $[\alpha]_D - 160.93^{\circ}$ at 20° ; the corresponding values obtained with natural nicotine are respectively $246.1-246.2^{\circ}$ under 730.5 mm. pressure, sp. gr. 1.0180 and 1.0097, and $[\alpha]_D - 166.39^{\circ}$ at 20° .

d-Nicotine was obtained by liberating the base from its syrupy *d*-ditartrate, and converting it by means of *l*-tartaric acid into *d*-nicotine *l*-ditartrate, which crystallises from water, melts at $88-89^{\circ}$, and has $[\alpha]_D - 25.58^{\circ}$ at 15° ; *d*-nicotine boils at $245.5-246.5^{\circ}$ under 729 mm. pressure, has a sp. gr. 1.0171 at $10^{\circ}/4^{\circ}$, 1.0094 at $20^{\circ}/4^{\circ}$, and $[\alpha]_D + 163.17^{\circ}$ at 20° .

Experiments made by Prof. A. Mayor to ascertain the relative poisoning effects of *d*- and *l*-nicotines are appended; it appears that *l*-nicotine is twice as poisonous as the *d*-base, and produces totally different symptoms.

W. A. D.

Composition of Yohimbine and its Relationship to Yohimboic Acid. LEOPOLD SPIEGEL [and ERNST B. AUERBACH] (*Ber.*, 1904, 37, 1759—1766. Compare *Abstr.*, 1899, i, 966; 1903, i, 274).—Crystallised yohimbine as obtained from plants loses a molecule of water forming *anhydroyohimbine*, $C_{22}H_{28}O_3N_2$; the salts of yohimbine are derived from the latter compound; thus the *nitrate*, $C_{22}H_{28}O_3N_2, HNO_3$, crystallises in large, colourless prisms melting at 276° . The following esters of yohimboic acid (noryohimbine) have been prepared: the *ethyl* ester crystallises in glistening needles melting at 189° , the *propyl* ester melts at $135-136^{\circ}$, and the *isobutyl* ester crystallises in platelets melting at $137-138^{\circ}$. These compounds contain two alkyl groups, one being attached to nitrogen; yohimboic acid is monobasic.

E. F. A.

A New General Reaction of Aldehydes. LOUIS J. SIMON and A. CONDUCHÉ (*Compt. rend.*, 1904, 138, 977—980).—Ethyl oxalacetate condenses readily with aldehydes in the presence of ammonia to form the ammonium salts of substituted derivatives of diketodihydropyrrolinecarboxylic acids, from which the free acid is liberated by hydrochloric acid. *Ethyl 2-phenyldiketodihydro-*

pyrroline-3-carboxylate, $\text{NH} \begin{array}{c} \text{CO} \text{---} \text{CO} \\ \diagdown \quad \diagup \\ \text{CHPh} \cdot \text{CH} \cdot \text{CO}_2\text{Et} \end{array}$, the compound formed by benzaldehyde, is a white, crystalline solid decomposing without melting at 185° , is slightly soluble in cold alcohol and less so in water, dissolves in cold concentrated acids, and is reprecipitated by water; gives a blue coloration when heated with fuming sulphuric acid; is neutral to litmus and acid to phenolphthalein, is soluble in dilute alkalis and in boiling alkali carbonates, and reprecipitated by dilute acids. The *potassium* and *silver* derivatives are described. The *copper* derivative, $(\text{C}_{13}\text{H}_{12}\text{O}_4\text{N})_2\text{Cu} \cdot 2\text{C}_2\text{H}_4\text{O}_2$, crystallises in characteristic green crystals containing 2 mols. of acetic acid, which it loses at 150° , is insoluble in water, but soluble in ammonia or concentrated nitric or acetic acid, and does not decompose at 200° . Both the acids and its salts develop a red coloration with ferric chloride, and the ketonic nature of the compound is displayed in the formation of a *phenylhydrazone* melting at $172\text{--}173^\circ$, and an *oxime* very soluble in alcohol and crystallising with water of crystallisation, the hydrated compound melting at 100° , the anhydrous at 150° .

The decomposition temperatures of similar compounds obtained with other aldehydes are as follows: with *m*-nitrobenzaldehyde, 173° ; with salicylaldehyde, 175° ; with anisaldehyde, 160° ; with vanillin, 180° ; and with piperonal, 155° .

The ammonia in this reaction can be replaced by a primary, but not by a secondary amine, the compound obtained by the interaction of ethyl oxalacetate, benzaldehyde, and aniline having the composition $\text{NPh} \begin{array}{c} \text{CO} \text{---} \text{CO} \\ \diagdown \quad \diagup \\ \text{CHPh} \cdot \text{CH} \cdot \text{CO}_2\text{Et} \end{array}$. [This compound has already been described by Schiff and Bertini. Compare Abstr., 1897, i, 293.]
M. A. W.

Compounds of Pyridine with Nitrates of Bivalent Metals. HERMANN GROSSMANN (*Ber.*, 1904, 37, 1253—1257).—*Copper nitrate pyridine*, $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{C}_5\text{H}_5\text{N}$, formed on adding a saturated solution of copper nitrate to an excess of pyridine, crystallises in strongly pleochroic pyramids and loses its pyridine on exposure to air.

The double salts, $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{C}_5\text{H}_5\text{N} \cdot 2\text{H}_2\text{O}$; $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{C}_5\text{H}_5\text{N} \cdot 2\text{H}_2\text{O}$; $\text{Mn}(\text{NO}_3)_2 \cdot 2\text{C}_5\text{H}_5\text{N} \cdot 2\text{H}_2\text{O}$, were obtained by adding pyridine to the aqueous solutions of the metallic nitrates and concentrating the solutions obtained over sulphuric acid. They have, in the sense of Werner's hypothesis, the general formula, $[\text{Me}(2\text{Py})(2\text{H}_2\text{O})](\text{NO}_3)_2$.

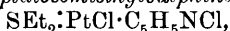
On dissolving cobalt bromide in pyridine, rose-coloured, microscopic, rhombic plates of the *salt* $\text{CoBr}_2 \cdot 4\text{C}_5\text{H}_5\text{N}$ separate; on dissolving it in hydrobromic acid and concentrating the solution, large, bluish-green, hygroscopic plates of *pyridinium cobalt bromide*,

$(\text{C}_5\text{H}_5\text{N})_2\text{CoBr}_4 \cdot 2\text{H}_2\text{O}$,
are obtained. The hexapyridine compound, $\text{CoBr}_2 \cdot 6\text{C}_5\text{H}_5\text{N}$, could not be isolated.
W. A. D.

Constitution of Platinum Bases. PETER KLASON (*Ber.*, 1904, 37, 1349—1360. Compare Abstr., 1903, i, 224).— *α -Platopyridine-ammine chloride*, $\text{C}_5\text{H}_5\text{N} \cdot \text{PtCl} \cdot \text{NH}_3\text{Cl}$, prepared from pyridine and

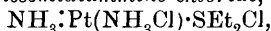
potassium platosemiammine chloride, or from ammonia and potassium platosemipyridine chloride, crystallises in yellow prisms and dissolves in 240 parts of water at the ordinary temperature.

Platosemipyridine-ethylsulphine chloride, $C_5H_5N:PtCl \cdot SEt_2Cl$, prepared from platosemiethylsulphine chloride and pyridine, melts at 96° , but when maintained in the fused state for a short time passes into the isomeric *platosemiethylsulphinepyridine chloride*,



melting at 160° . The latter compound is also obtained from potassium platosemipyridine chloride and ethyl sulphide. Silver nitrate converts it into a third isomeride, *platosemipyridinesemiethylsulphine chloride*, $SEt_2Cl \cdot Pt \cdot C_5H_5NCl$, crystallising from alcohol or chloroform in colourless needles, and melting and decomposing at 165° . A mixture of the first two isomerides is obtained by the action of pyridine on α - or β -platoethylsulphine chloride.

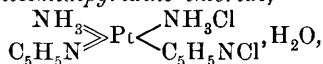
Platosemiethylsulphinesemidiammine chloride,



prepared from α -platosemidiammine chloride and ethyl sulphide, could not be obtained in a crystalline form. Its solution passes partially into the isomeric platosemiamminesemiethylsulphineammine chloride, $SEt_2 : Pt(NH_3Cl)_2$.

β -Platosemidiammine chloride and ethyl sulphide form the unstable platosemiamminesemiethylsulphineammine chloride.

Platosemidiamminesemidipyridine chloride,



obtained in solution by Jørgensen (Abstr., 1886, 857), crystallises in cauliflower-like, readily soluble masses.

The paper also contains a theoretical discussion of the isomerism and tautomerism of the platinum bases.

C. H. D.

2:6-Lutidine-3:5-dicarboxylic Acid. ERNST MOHR and W. SCHNEIDER (*J. pr. Chem.*, 1904, 69, 245—255).—2:6-Dimethylpyridine-3:5-dicarboxylic acid (Engelmann, Abstr., 1886, 259) was obtained by preparing ethylic dihydrolutidinecarboxylate (Knoevenagel and Klages, Abstr., 1895, i, 51), oxidising it in suspension in alcohol at 40° with nitrous anhydride (or, on a smaller scale, by warming it with 1.1 mols. of 20—25 per cent. nitric acid), and hydrolysing the re-ulting ester with 1.35 times the calculated amount of alcoholic potassium hydroxide. The acid was purified by crystallisation from water and by passage through the silver salt; it then gave satisfactory numbers on analysis, corresponding with an anhydrous acid (not one with $\frac{1}{2}H_2O$). The pure acid melts at 315° to 320° according to the rapidity of heating; 1 part dissolves in 97—98 parts of boiling, and in about 3250 of cold water; in 150—160 of boiling and in about 290 of cold alcohol.

C. F. B.

α - and γ -Phenylpyridylcarbinols. ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1904, 37, 1370—1372).—Zinc dust and sodium ethoxide reduce α - and γ -phenyl pyridyl ketones (2- and 4-benzoylpyridines) (Abstr., 1902, i, 175) to the corresponding carbinols.

Phenyl-2-pyridylcarbinol, $C_5NH_4 \cdot CHPh \cdot OH$, separates from benzene on addition of light petroleum in large, transparent crystals, melts at 82° , and dissolves very readily in alcohol, ether, or benzene. Dilute acids dissolve it, and it is reprecipitated on addition of alkali. The sparingly soluble *platinichloride* crystallises in orange-red leaflets and melts and decomposes at 197° .

Phenyl-4-pyridylcarbinol separates from benzene or ethyl acetate in small, white crystals, melts at 126° , and dissolves readily in alcohol, sparingly in ether or benzene. The sparingly soluble *platinichloride* crystallises in orange scales and melts at 205° .

Alkaline potassium permanganate oxidises both carbinols to the original ketones. C. H. D.

Oxidation of Benzylated and Phenylated Pyridines. ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1904, 37, 1373—1374).—When benzylpyridines (Abstr., 1903, i, 853) are oxidised by potassium permanganate in acid solution, the benzene ring is destroyed and pyridinecarboxylic acids are formed; in neutral solution, however, the pyridine ring is attacked, with the formation of benzoic acid (Abstr., 1901, i, 484). Similar results were obtained by Skraup and Cobenzl in the oxidation of 3-phenylpyridine (Abstr., 1883, 1010).

When a mixture of 2- and 4-phenylpyridines prepared by the action of solid sodium nitrite and acetic acid on a mixture of aniline and pyridine (compare Möhlau and Berger, Abstr., 1893, i, 701) is oxidised with potassium permanganate in neutral or alkaline solution, benzoic acid is obtained. In acid solution, *isonicotinic* and *picolinic* acids are obtained. These results are in accordance with Vorländer's rule (Abstr., 1901, i, 454) that compounds with tervalent nitrogen pass into saturated compounds with quinquivalent nitrogen in acid solution. C. H. D.

Condensation of 2- and 4-Benzylpyridines with Formaldehyde. ALEXEI E. TSCHITSCHIBABIN (*J. pr. Chem.*, 1904, [ii], 69, 310—320. Compare Stoehr, Abstr., 1892, 628; Koenigs and Happe, Abstr., 1903, i, 850).—When heated with 40 per cent. formaldehyde at 150° , but not at 100° , 2-benzylpyridine is converted into phenyl-2-pyridyl-dimethylolmethane and α -phenyl- α -2-pyridylethylene.

Phenyl-2-pyridyldimethylolmethane, $C_5NH_4 \cdot CPh(CH_2OH)_2$, crystallises in needles and melts at 106 — 107° . The *platinichloride*, $(C_{14}H_{15}O_2N)_2 \cdot H_2PtCl_6$, crystallises in needles; the *picrate* is a yellow, crystalline powder and melts at 180° .

α -*Phenyl- α -2-pyridylethylene*, $C_5NH_4 \cdot CPh \cdot CH_2$, is a viscid oil, which distils at 292 — 295° with slight decomposition, is soluble in dilute mineral acids, and forms an additive compound with bromine. The *picrate*, $C_{13}H_{11}N, C_6H_3O_7N_3$, crystallises in long, glistening, yellow prisms and melts at 155° ; the *platinichloride* forms large, red leaflets and melts at 175° ; the mother liquor from the *picrate* contains a small quantity of a substance, probably methylolphenylpyridylmethane.

2-Benzylpyridine and formaldehyde yielded a slight amount of α -phenyl- α -2-pyridylethylene when exposed to direct sunlight for

3 weeks. When heated with 40 per cent. formaldehyde at 100°, 4-benzylpyridine forms phenyl-4-pyridyldimethylolmethane, phenyl-4-pyridylmethylolmethane, and α -phenyl- α -4-pyridylethylene; at 50°, phenyl-4-pyridyldimethylolmethane only is formed; on exposure to direct sunshine for 15 days, the glycol and a trace of the ethylene compound are obtained.

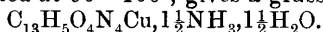
Phenyl-4-pyridyldimethylolmethane, $C_5NH_4 \cdot CPh(CH_2 \cdot OH)_2$, crystallises in delicate needles and melts at 194°. The *platinichloride*, $(C_{14}H_{15}O_2N)_2 \cdot H_2PtCl_6$, forms small, glistening, orange-red crystals and melts at 185°.

Phenyl-4-pyridylmethylolmethane, $C_5NH_4 \cdot CHPh \cdot CH_2 \cdot OH$, crystallises in prisms or leaflets and melts at 89—90°. The *platinichloride*, $(C_{13}H_{13}ON)_2 \cdot H_2PtCl_6$, forms red crystals and melts at 160°. 4-Benzoylpyridine is formed by oxidation of phenyl-4-pyridylmethylolmethane with potassium permanganate.

α -*Phenyl α -4-pyridylethylene*, $C_{13}H_{11}N$, is an oil which boils at 300—305° and forms an additive compound with bromine. The *platinichloride*, $(C_{13}H_{11}N)_2 \cdot H_2PtCl_6$, crystallises in delicate, yellow needles and melts at 182—185°. G. Y.

Condensation Products of the Three Nitrobenzaldehydes [with Ethyl Cyanoacetate in presence of Ammonia]. GIOVANNI ISSOGLIO (*Atti R. Accad. Sci. Torino*, 1904, 39, 140—160. Compare Guareschi, *Abstr.*, 1898, i, 274, and 1902, i, 52).—The ammonium derivative of 3:5-dicyano-6-hydroxy-4-m-nitrophenyl- $\Delta^{3,6}$ -dihydropyridone, $N \begin{matrix} \diagup C(OH_4) \cdot CH(CN) \\ \diagdown CO \quad \quad \quad C(CN) \end{matrix} > C \cdot C_6H_4 \cdot NO_2$, is the principal product

when *m*-nitrobenzaldehyde is condensed with ethyl cyanoacetate and ammonia at the ordinary temperature; it crystallises from hot water in slightly yellow prisms, does not melt at 300°, and when warmed with dilute sulphuric acid gives β -*m*-nitrophenylcyanovinylacetic acid, $NO_2 \cdot C_6H_4 \cdot C(:CH \cdot CN) \cdot CH_2 \cdot CO_2H$. On decomposing the barium or silver salt corresponding with the foregoing ammonium derivative with cold dilute sulphuric acid or hydrogen sulphide respectively, 3:5-dicyano-6-hydroxy-4-m-nitrophenyl- $\Delta^{3,6}$ -dihydropyridone is obtained; it is very soluble in water, alcohol, acetic acid, and ethyl acetate, melts and decomposes at 260°, and gives a silver derivative, $C_{13}H_5O_4N_4Ag \cdot 4H_2O$, a barium derivative, $(C_{13}H_5O_4N_4)_2Ba \cdot 7H_2O$, and a bluish-green cuprammonium compound, $C_{13}H_5O_4N_4Cu \cdot 2NH_3 \cdot 3H_2O$; the latter, when heated at 90—100°, gives a grass-green salt,



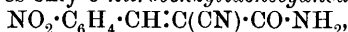
Together with the foregoing pyridone, *m*-nitrobenzylcyanoacetamide, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CH(CN) \cdot CO \cdot NH_2$, is formed; it crystallises from water or alcohol in white, silky needles, melts at 147—148°, and on hydrolysis with aqueous barium hydroxide gives *m*-nitrobenzylmalonic acid. A compound,

$NO_2 \cdot C_6H_4 \cdot CH : C(CN) \cdot CO \cdot NH_2$, $NO_2 \cdot C_6H_4 \cdot CH : C(CN) \cdot CO_2Et$, similar to Carrick's salt (*Abstr.*, 1892, 1086), was also isolated from the condensation; it crystallises from alcohol and melts at 186.5°.

3:5-Dicyano-6-hydroxy-4-p-nitrophenyl- $\Delta^{3,6}$ -dihydropyridone, prepared in the same way as the analogous *m*-nitro-compound, crystallises from alcohol in prismatic needles, melts and decomposes at 270—275°.

and gives a crystalline *barium* derivative, $(C_{13}H_5O_4N_4)_2Ba, 6H_2O$, and an *ammonium* derivative with $1\frac{1}{2}H_2O$. *p*-Nitrobenzylcyanoacetamide crystallises from dilute alcohol in colourless needles melting at 168.5° . The *p*-nitro-compound, $C_{22}H_{17}O_7N_5$, corresponding with Carrick's compound, separates from alcohol of 90° in small, white, silky prisms and melts at 194 — 195° .

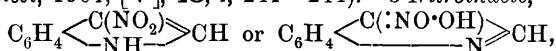
On condensing *o*-nitrobenzaldehyde with ammoniacal ethyl cyanoacetate, an entirely different reaction ensues from that occurring in the case of the meta- and para-compounds. A large proportion of resin is formed and small quantities of *o*-azoxybenzoic acid (?) and trinitrohydrobenzamide, $NO_2 \cdot C_6H_4 \cdot CH(N:CH \cdot C_6H_4 \cdot NO_2)_2$, are produced. With cyanoacetamide, *o*-nitrobenzaldehyde in presence of dilute ammonia gives only *o*-nitrobenzylidenecyanoacetamide,



which crystallises from dilute alcohol in long, silky needles and melts at 173 — 174° .

W. A. D.

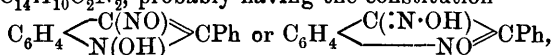
Nitroindoles. FRANCESCO ANGELICO and G. VELARDI (*Atti R. Accad. Lincei*, 1904, [v], 13, i, 241—244).—3-Nitroindole,



which cannot be obtained from indole by nitration with nitric acid, is easily prepared by the action of ethyl nitrate and sodium ethoxide on indole dissolved in absolute ether; it crystallises from benzene in yellow needles and melts at 210° . 3-Nitro-2-methylindole, obtained similarly from 2-methylindole, is identical with the compound formed by the oxidation of 3-nitro-*o*-2-methylindole (Abstr., 1901, i, 45), and, on further nitration with nitric acid, gives Zatti's dinitromethylindole (Abstr., 1890, 897); on oxidation with potassium permanganate, 3-nitroindole-2-carboxylic acid, $C_6H_4 \begin{array}{c} \diagup C(NO_2) \diagdown \\ \text{---} NH \text{---} \end{array} C \cdot CO_2H$, is obtained, which crystallises from xylene in intensely yellow spangles and melts and decomposes at 230° , giving a sublimate consisting of 3-nitroindole.

W. A. D.

Nitrosoindoles. ANGELO ANGELI and FRANCESCO ANGELICO (*Atti R. Accad. Lincei*, 1904, [v], 13, i, 255—258. Compare Angeli and Spica, Abstr., 1899, i, 938; Angelico and Calvello, 1901, i, 747; 1904, i, 188).—When 1-hydroxy-2-phenylindole, $C_6H_4 \begin{array}{c} \diagup CH \diagdown \\ \text{---} N(OH) \text{---} \end{array} CPh$ (Fischer and Hütz, Abstr., 1895, i, 371), is caused to interact with amyl nitrite in alcoholic solution containing sodium ethoxide, a substance $C_{14}H_{10}O_2N_2$, probably having the constitution



is obtained; it melts at 240° , gives an acetyl, benzoyl, and ethyl derivative, and on reduction with zinc and acetic acid is converted into 3-amino-2-phenylindole. It is easily converted, by the removal of oxygen, into 3-isonitroso-2-phenylindole, $C_6H_4 \begin{array}{c} \diagup C(NOH) \diagdown \\ \text{---} N \text{---} \end{array} CPh$, and can be oxidised to a substance $C_{14}H_9O_2N$, which sublimes in lustrous

red plates, has the properties of a quinone, and possibly is to be represented by the formula $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{NO} \end{smallmatrix} \text{NPh}$, since with hydroxylamine it gives *isonitrosophenylindole*. W. A. D.

A New Class of Dyes obtained from Quinoline-2-carboxylic Acids. EMIL BESTHORN and J. IBELE (*Ber.*, 1904, 37, 1236—1243).—When quinoline-2-carboxylic acid is heated with acetic anhydride for half an hour at 130—135°, a substance $C_{19}H_{12}ON_2$ is obtained which crystallises from absolute alcohol in red, pleochroic needles, sinters at 200°, and melts indefinitely at 230—240°; in solution, it is fluorescent and remarkably sensitive to light, the colour of a saturated benzene solution disappearing when exposed to bright sunshine in a few minutes. The composition of the substance would correspond with that of a 2:2'-diquinolyl ketone, $CO(C_9H_6N)_2$, and in agreement with this structure it is converted by boiling hydrobromic acid into quinoline and quinoline-2-carboxylic acid, and by sulphuric acid into quinoline-2-carboxylic acid and carbostyryl; on the other hand, it is a feeble base, and does not interact with hydroxylamine or phenylhydrazine. Attempts to prepare 2:2'-diquinolyl ketone by heating calcium quinoline-2-carboxylate gave only 2:7'-diquinolyl.

The same substance, $C_{19}H_{12}ON_2$, is also formed on heating quinoline-2-carboxylic acid with benzoic anhydride at 140°, but anhydrides of dibasic acids, such as phthalic or succinic anhydrides, act differently. W. A. D.

4-Quinolylacrylic Acid and 4-Quinolylpropionic Acid. WILHELM KOENIGS and ALFRED MÜLLER (*Ber.*, 1904, 37, 1337—1340).—Alcoholic potassium hydroxide converts chloral-lepidine into *quinolyl-4-acrylic acid*, $C_9NH_6 \cdot CH:CH \cdot CO_2H$, which crystallises from a mixture of alcohol and acetic acid in small, white needles and melts and decomposes at 250—255°. The *hydrochloride* forms long, felted needles. The *platinichloride* forms yellow needles containing $1\frac{1}{2}H_2O$ and becomes anhydrous at 120°.

Hydriodic acid reduces *quinolyl-4-acrylic* to *quinolyl-4-propionic acid*, $C_9NH_6 \cdot CH_2 \cdot CH_2 \cdot CO_2H$, which crystallises from water in white needles, melts at 202—203°, and dissolves readily in alcohol or hot acetone. The *copper* salt forms characteristic violet-blue crystals. The *platinichloride* forms yellow tablets.

Sodium reduces the alcoholic solution of 4-quinolylpropionic acid to 4-tetrahydroquinolylpropionic acid, which darkens in the air and melts at 217—218°. The *nitroso*-compound, $NO \cdot C_9NH_6 \cdot CH_2 \cdot CH_2 \cdot CO_2H$, crystallises from ether in faintly yellow cubes, melts and decomposes at 121—122°, and dissolves readily in ether or alcohol. C. H. D.

Derivatives of 2:4-Dimethylquinoline and 2:4:6-Tri-methylpyridine. WILHELM KOENIGS and ALFRED MENGEL (*Ber.*, 1904, 37, 1322—1337).—Acetylacetone anilide, described by Coombes (*Abstr.*, 1888, 504) as a liquid, crystallises from light petroleum in colourless leaflets, melts at 51—53°, and boils at 279—281° (uncorr.) under 715 mm. pressure. Concentrated sulphuric acid converts it into 2:4-dimethylquinoline.

Formaldehyde reacts with an excess of 2:4-dimethylquinoline to form 4-methyl-2- β -hydroxyethylquinoline, $\text{OH}\cdot\text{C}_2\text{H}_4\cdot\text{C}_9\text{NH}_5\text{Me}$, separating from ethyl acetate in white crystals and melting at 98° . The *hydrochloride* is anhydrous and melts at 193 – 194° , the *platinichloride* forms orange needles and melts and decomposes at 210 – 211° , the *picrate* forms small, yellow needles and melts at 164 – 166° . Nitric acid oxidises the base to 4-methylquinoline-2-carboxylic acid, separating from water as a crystalline, yellow powder containing $1\frac{1}{2}\text{H}_2\text{O}$, which is evolved at 105° , the acid then melting at 153 – 154° . The *platinichloride* forms yellowish-red crystals containing H_2O , blackens at 200° , and melts and decomposes at 210 – 212° . The *hydrogen sulphate* and *hydrochloride* form white crystals. The readily soluble ammonium salt separates from water in large, feathery crystals. The acid decomposes into carbon dioxide and lepidine at 170 – 180° .

2:4-Dimethylquinoline and formaldehyde also react to form 4-methyl-2- α - γ -dihydroxyisopropylquinoline, $\text{CH}(\text{CH}_2\cdot\text{OH})_2\cdot\text{C}_9\text{NH}_5\text{Me}$, crystallising from ethyl acetate in slender needles, sintering at 135° , and melting at 140° . The *hydrochloride* forms a white, crystalline powder and melts at 194° , the *platinichloride* forms reddish-yellow needles containing H_2O , becomes anhydrous at 110 – 120° , and melts and decomposes at 172° .

No higher condensation product with formaldehyde could be obtained in a crystalline condition.

Chloral-2:4-dimethylquinoline, $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{C}_9\text{NH}_5\text{Me}$, from chloral and dimethylquinoline in amyl acetate solution, forms colourless crystals and melts at 126° . The sparingly soluble *hydrochloride* melts at 154° . Alcoholic potassium hydroxide converts the base into 4-methylquinoline-2-acrylic acid, $\text{C}_9\text{NH}_5\text{Me}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$, crystallising from alcohol in slender, yellow needles and melting at 214° . The *platinichloride* forms reddish-yellow needles and melts above 300° . Potassium permanganate oxidises 4-methylquinoline-2-acrylic acid to 4-methylquinoline-2-carboxylic acid and oxalic acid.

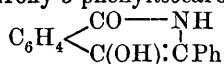
Acetylacetone-p-anisidine crystallises from light petroleum in white tablets and melts at 49° . It was not found possible to convert it into the corresponding quinoline derivative by means of dehydrating agents.

5-Methoxy-2:4-dimethylquinoline is best prepared by condensing paraldehyde with acetone by means of hydrogen chloride and combining the product with *p*-anisidine. It crystallises in colourless needles containing $2\text{H}_2\text{O}$ and melts at 92° . The *picrate* forms felted, yellow needles and melts at 221° , the *platinichloride* forms orange needles and melts at 241° , the *sulphate* forms slender needles and melts and decomposes at 242° , the *chromate* forms brown needles and decomposes at 188° without melting. The solution of the base in very dilute sulphuric acid shows a strong blue fluorescence, and gives a green coloration with chlorine water and ammonia. The *phthalone* crystallises from alcohol in reddish-yellow needles and melts at 272° .

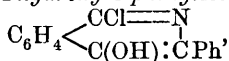
Chloral-2:4:6-trimethylpyridine (chloral-collidine) crystallises from acetone and melts at 139.5° . A condensation product with more than 1 mol. of chloral could not be prepared.

C. H. D.

4-Hydroxyisocarbostyryl. ARTHUR ULRICH (*Ber.*, 1904, 37, 1685—1696. Compare *Abstr.*, 1900, i, 359).— α -Phthalyliminophenylacetic acid, $C_8H_4O_2:N\cdot CHPh\cdot CO_2H$, prepared by the action of phthalic anhydride on aminophenylacetic acid, crystallises in pointed, rhombic leaflets and melts at 168° . The ethyl ester crystallises in ball-like aggregates of colourless leaflets, melts at 99° , and by sodium methoxide is converted into 4-hydroxy-3-phenylisocarbostyryl,



(Gabriel, *Abstr.*, 1886, 266; 1887, 61), which is reduced by hydriodic acid and phosphorus at 190° to phenylisocarbostyryl. α -Phthaloylaminophenylacetic acid, $CO_2H\cdot C_6H_4\cdot CO\cdot NH\cdot CHPh\cdot CO_2H$, is formed by the action of sodium methoxide on ethyl α -phthalylaminophenylacetate in aqueous-alcoholic solution. 4-Methoxy-3-phenylisocarbostyryl (Gabriel, *Ber.*, 1887, 20, 2867), formed by the action of sodium methoxide and methyl iodide in methyl-alcoholic solution on 4-hydroxy-3-phenylisocarbostyryl, melts at 240° and is reconverted into hydroxyphenylisocarbostyryl by the action of boiling hydrobromic acid. 1-Chloro-4-hydroxy-3-phenylisoquinoline,



is formed along with a small quantity of 1:4-dichloro-3-phenylisoquinoline by the action of phosphorus oxychloride on 4-hydroxy-3-phenylisocarbostyryl at 150 — 160° . It crystallises in transparent prisms, melts at 119° , is soluble in dilute cold aqueous potassium or sodium hydroxide solutions, but not in dilute ammonia.

1-Chloro-4-methoxy-3-phenylisoquinoline, $C_6H_4 \begin{array}{l} \text{CCl} \text{---} \text{N} \\ \text{C}(\text{OMe}) \text{---} \end{array} >CPh$, is formed by the action of phosphorus oxychloride on 4-methoxy-3-phenylisocarbostyryl, and by the action of methyl iodide and sodium methoxide on 1-chloro-4-hydroxy-3-phenylisoquinoline. It crystallises in prisms, melts at 103.5° , and is isomeric with 4-chloro-1-methoxy-3-phenylisoquinoline, which melts at 76° (Gabriel, *Abstr.*, 1887, 61).

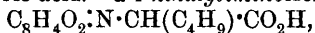
4-Ethoxy-3-phenylisocarbostyryl crystallises in stellate clusters of rose-coloured needles and melts at 183° . 1-Chloro-4-ethoxy-3-phenylisoquinoline melts at 83.25° .

4-Methoxy-3-ethylisocarbostyryl, $C_6H_4 \begin{array}{l} \text{CO} \cdot \text{NH} \\ \text{C}(\text{OMe}) \text{---} \end{array} >CEt$, obtained from 4-hydroxy-3-ethylisocarbostyryl (*Abstr.*, 1900, i, 359), crystallises in stellate clusters of needles and melts at 160 — 160.5° . 1-Chloro-4-methoxy-3-ethylisoquinoline crystallises in colourless, hexagonal leaflets and melts at 55.5° . 1-Chloro-4-hydroxy-3-ethylisoquinoline crystallises in clusters of quadratric prisms and melts at 125.25° .

Ethyl α -phthalyliminoisovalerate, $C_8H_4O_2:N\cdot CH(CHMe_2)\cdot CO_2Et$, prepared by the action of potassium phthalimide on ethyl α -bromoisovalerate, is a yellow liquid, which boils at 211° under 36.6 mm. pressure. Sodium methoxide converts it into 4-hydroxy-3-isopropylisocarbostyryl,

$C_6H_4 \begin{array}{l} \text{CO} \text{---} \text{NH} \\ \text{C}(\text{OH}) \text{---} \end{array} :CPr^s$, which crystallises in colourless

tetrahedra and melts at 198—207°. It is soluble in dilute sodium hydroxide solution, from which it is precipitated by ammonium chloride or hydrochloric acid. *α-Phthalyliminoisohexzoic acid*,



is formed by the action of phthalic anhydride on leucine. It crystallises in rhombic leaflets and melts at 141·5—142°. The *methyl* ester melts at 65·5—66°, and, when acted on by sodium methoxide, yields 4-hydroxy-3-isobutylisocarbostyryl, which melts at 171—173°. G. Y.

Combination of *o*-Nitrobenzaldehyde with Phenol in presence of Hydrochloric Acid. ALFRED GUYOT and ALBERT HALLER (*Bull. Soc. chim.*, 1904, 31, 530—533).—When a mixture of *o*-nitrobenzaldehyde and phenol, dissolved in acetic acid, is heated at 100° with hydrochloric acid, a product $\text{C}_{13}\text{H}_8\text{O}_2\text{NCl}$ is formed, which may have the constitution $\text{C}_6\text{H}_3\text{Cl} \begin{smallmatrix} \text{NH} \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_3\cdot\text{OH}$. It is crystalline, melts and sublimes at 200°, and is soluble in alcohol. On the addition of a drop of alkali to its alcoholic solution, a magnificent green fluorescence is produced. With silver nitrate, followed by a drop of ammonia, the alcoholic solution gives a crystalline, vermilion-coloured precipitate of the *silver* derivative. The *methyl ether*, obtained by the action of methyl iodide in closed tubes at 100°, crystallises in long, yellow needles and melts at 144°; the *benzyl ether*, produced by warming alkaline solutions of the condensation product with benzyl chloride, forms fine crystals and melts at 142°; the *benzoyl* derivative occurs in small crystals and melts at 231°.

This condensation product has also been described by Siebert (*Inaug. Diss. Marburg*, July, 1903), who ascribed to it the formula $\text{C}_6\text{H}_3\text{Cl} \begin{smallmatrix} \text{C} \\ \text{N} \end{smallmatrix} \text{O} \text{C}_6\text{H}_4\cdot\text{OH}$.

T. A. H.

Preparation of Acridine Dyes. ANILINFARBEN- and EXTRAKT-FABRIKEN VORM. J. R. GEIGY (D.R.-P. 149409 and 149410).—Orange-yellow dyes of the acridine series are obtained by heating formyl derivatives of *m*-diamines (Abstr., 1903, i, 522) or the formyl derivatives of aromatic amines and alkylated amines, and many other formyl derivatives of aromatic bases, with ammonium salts or salts of organic bases at 150—200°. The salts appear to act only as condensing agents, and their nature is without effect on the character of the product. The solutions of the dyes in water, alcohol, or concentrated sulphuric acid are fluorescent, but less so than solutions of acridine yellow.

C. H. D.

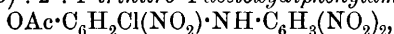
A New Base from *p*-Phenylenediamine. LUDWIG PAUL (*Zeit. angew. Chem.*, 1904, 17, 589—591).—The author endeavours to ascertain the conditions under which the base previously prepared by him from impure *p*-phenylenediamine (*ibid.*, 1897, 10) may be prepared from pure *p*-phenylenediamine.

A. McK.

Chloronitro- and Nitro-derivatives of 4-Hydroxy-2':4'-dinitrodiphenylamine. FRÉDÉRIC REVERDIN and ERNST DELÉTRA (*Ber.*, 1904, 37, 1727—1732. Compare Abstr., 1903, i, 248, 857).—3:2':4'-Trinitro-4-aminodiphenylamine, obtained from 1-chloro-2:4-

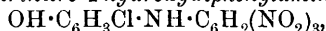
dinitrobenzene and *o*-nitro-*p*-phenylenediamine, crystallises in small, reddish-brown needles, melts at 226°, and is probably identical with the base described by the Farbwerke Höchst (D.R.-P. 1899, 110360). When treated with sodium chlorate and hydrochloric acid, it yields the 2 : 3 : 5- or 2 : 3 : 6-trichloroquinone-2' : 4'-dinitrophenylimide, which melts at 211°, together with a *tetrachloroquinone*-2' : 4'-dinitrophenylimide.

3-Chloro-2 (or 6) : 2' : 4'-trinitro-4-acetoxydiphenylamine,



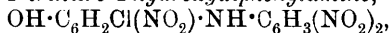
is obtained by acting with fuming nitric acid on 3-chloro-2' : 4'-dinitro-4-acetoxydiphenylamine. It crystallises in needles, melts at 177.5—178°, and is hydrolysed to 3-chloro-2 (or 6) : 2' : 4'-trinitro-4-hydroxydiphenylamine, which melts at 252°.

3-Chloro-2' : 4' : 6'-trinitro-4-hydroxydiphenylamine,



obtained from 2-chloro-4-aminophenol and picryl chloride, forms dark red, prismatic crystals and melts at 185.5°. The *acetyl* derivative crystallises in orange-coloured prisms and melts at 173°.

3-Chloro-5 : 2' : 4'-trinitro-4-hydroxydiphenylamine,



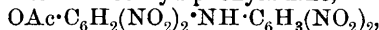
obtained from 2-chloro-6-nitro-4-aminophenol (D.R.-P. 1903, 11458) and chlorodinitrobenzene, crystallises in matted, golden needles and melts at 232°. The *acetyl* derivative crystallises in brown prisms and melts at 188.5°.

2-Chloro-2' : 4'-dinitro-4-acetoxydiphenylamine yields a *mononitro*-derivative, $\text{OAc} \cdot \text{C}_6\text{H}_2\text{Cl}(\text{NO}_2) \cdot \text{NH} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2$, which crystallises from acetone in lemon-yellow prisms, containing acetone of crystallisation, and after heating at 100° melts at 134.5°. On hydrolysis with sodium hydroxide, a gelatinous *sodium* derivative is formed, which, with hydrochloric acid, yields *nitro-2-chloro-2' : 4'-dinitro-4-hydroxydiphenylamine*. This crystallises in yellow, prismatic needles and melts at 232.5°.

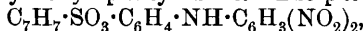
3 : 5-Dichloro-2' : 4'-dinitro-4-acetoxydiphenylamine yields a *mononitro*-derivative which melts at 177.5°; the corresponding *hydroxy*-compound, $\text{OH} \cdot \text{C}_6\text{H}_4\text{Cl}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2$, crystallises in orange-coloured prisms and melts at 235°; the *sodium* derivative forms glistening, red leaflets.

3 : 5-Dichloro-2' : 4' : 6'-trinitro-4-hydroxydiphenylamine, obtained from picryl chloride and 2 : 6-dichloro-4-aminophenol, crystallises in glistening, brown prisms and melts at 225°. The *acetyl* derivative forms greenish-yellow leaflets and melts at 259°.

Dinitro-2' : 4'-dinitro-4-acetoxydiphenylamine,

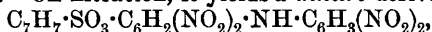


obtained by nitration of 2' : 4'-dinitro-4-acetoxydiphenylamine, crystallises in large, brownish-yellow prisms or yellow needles and melts at 161°; the *hydroxy*-compound crystallises in lemon-yellow needles and melts at 225.5°; the *sodium* compound is gelatinous. The same dinitro-2' : 4'-dinitro-4-hydroxydiphenylamine is obtained by successive nitration and hydrolysis of the dinitrophenylether or the *p*-tolylsulphonate of 2' : 4'-dinitro-4-hydroxydiphenylamine. The *p*-tolylsulphonate,



obtained from *p*-tolylsulphonic chloride and 2' : 4'-dinitro-4-hydroxy-

diphenylamine, crystallises in yellow leaflets or prismatic needles and melts at 178.5°. On nitration, it yields a dinitro-derivative,



which crystallises in delicate, lemon-yellow needles and melts at 189.5°. The dinitro-derivative of the dinitrophenyl ether of 2':4'-dinitro-4-hydroxydiphenylamine crystallises in brownish-yellow leaflets and melts at 233°.

G. Y.

Tolylenediaminesulphonic Acids. CARL BÜCKEL (*Zeit. Farb. Text. Chem.*, 1904, 3, 137—139).—The acid obtained by Wiesinger (this Journ., 1874, 805) on sulphonating *m*-tolylenediamine is shown to be identical with Foth's acid (Abstr., 1886, 152), prepared from *o*-nitro-*p*-toluidine; it has therefore the structure $[\text{Me}:(\text{NH}_2)_2:\text{SO}_3\text{H} = 1:2:4:5]$.

The acid $[\text{Me}:(\text{NH}_2)_2:\text{SO}_3\text{H} = 1:2:4:6]$ mentioned in Oehler's Patent (D.R.-P. 51662) is prepared by nitrating with a mixture of fuming nitric and sulphuric acids the acid obtained on sulphonating *p*-nitrotoluene, and subsequently reducing the dinitrotoluenesulphonic acid with zinc and hydrochloric acid; the hydrochloride of the diamino-toluenesulphonic acid crystallises from water, but is gradually dissociated by repeated crystallisation, forming the sulphonic acid itself.

The acid $[\text{Me}:(\text{NH}_2)_2:\text{SO}_3\text{H} = 1:2:6:4]$ is best obtained by Schwanert's method (this Journ., 1877, ii, 471). The three acids are distinguished by the nature of the azo-dyes they give with diazotised *p*-toluidine, *o*-toluidine, and *o*-tolidine. For details, the original should be consulted.

W. A. D.

Constitution of *o*-Tolidine. GUSTAV SCHULTZ, GEORG ROHDE, and F. VICARI (*Ber.*, 1904, 37, 1401—1402).—The hydrocarbon obtained by the elimination of the amino-groups from *o*-tolidine is identical with the compound obtained by the action of sodium on *m*-iodotoluene, and must therefore be 3:3'-dimethyldiphenyl; the constitution of *o*-tolidine, therefore, is $\text{NH}_2 \cdot \text{C} \begin{smallmatrix} \text{CMe} \cdot \text{CH} \\ \text{CH} - \text{CH} \end{smallmatrix} \text{C} \begin{smallmatrix} \text{CH} \cdot \text{CMe} \\ \text{CH} - \text{CH} \end{smallmatrix} \text{C} \cdot \text{NH}_2$.

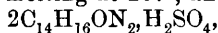
J. J. S.

Some Amino- and Aminohydroxy-diphenylamines. ROBERT GNEHM [with G. WEBER] (*J. pr. Chem.*, 1904, [ii], 69, 223—244).—Dimethyl-*p*-diaminodiphenylamine (Abstr., 1903, i, 831) can also be prepared by heating dimethyl-*p*-phenylenediamine with *p*-aminophenol and a little zinc chloride at 150° in an atmosphere of carbon dioxide; its hydrochloride, $\text{C}_{14}\text{H}_{17}\text{N}_3 \cdot 2\text{HCl}$, and sulphate, $\text{C}_{14}\text{H}_{17}\text{N}_3 \cdot \text{H}_2\text{SO}_4$, were analysed; it forms a triacetyl derivative, melting at 142°. When boiled in alcoholic solution with 1-chloro-2:4-dinitrobenzene and sodium acetate, it yields a condensation product, $\text{C}_{20}\text{H}_{19}\text{O}_4\text{N}_5$, melting at 209°. When added gradually to a mixture of sulphur and phenol heated at 200—250°, it forms an amorphous sulphuretted colouring-matter.

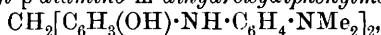
Dimethyltriaminodiphenylamine, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_6\text{H}_3(\text{NH}_2)_2$, is obtained by reducing *p*-nitrosodimethylaniline hydrochloride in aqueous solution with zinc dust, adding *m*-phenylenediamine, oxidising with sodium hypochlorite solution at 0°, filtering off the indamine which is

precipitated, and reducing it in solution in dilute acetic acid with zinc dust; it crystallises with difficulty, melts at 70–75°, oxidises readily in the air, and yields a sulphuretted colouring-matter.

Dimethyl-*p*-amino-*m*-hydroxydiphenylamine (*loc. cit.*) forms a *hydrochloride*, $C_{14}H_{16}ON_2 \cdot HCl$, melting at 207°, and a *sulphate*,



melting at 193°; when boiled with methyl iodide and sodium hydroxide in methyl alcoholic solution, it forms a *methiodide*, $C_{14}H_{16}ON_2 \cdot MeI$, which melts at 199.5–200°; the *ethiodide* melts at 180°. The nitrosoamine, when allowed to remain with alcoholic hydrochloric acid at 0°, becomes transformed into reddish-brown *p*-nitrosodimethyl-*p*-amino-*m*-hydroxydiphenylamine, $C_{14}H_{15}O_2N_3$, melting at 164°; this is reduced by alcoholic ammonium sulphide to the corresponding *amine*, $C_{14}H_{17}ON_3$, and with *p*-nitrobenzyl cyanide, it yields a reddish-brown *azomethine* derivative, $C_{22}H_{19}O_3N_5$, melting at 213–214°. With formaldehyde, 1 mol. of the original base condenses in alcoholic hydrochloric acid solution to amorphous *dimethyl-p-aminophenylamino-m-hydroxybenzyl alcohol*, $NMe_2 \cdot C_6H_4 \cdot NH \cdot C_6H_3(OH) \cdot CH_2 \cdot OH$, which does not melt at 360°; 2 mols. condense to amorphous *tetramethyl-p-diamino-p-diphenyl-p-diamino-m-dihydroxydiphenylmethane*,



melting at about 150°, which, when oxidised together with dimethylaniline in acid solution, yields a green triphenylmethane *dye*, $C_{29}H_{32}O_2N_4$. The original base yields a sulphuretted colouring-matter.

2-*p*-Dimethylanilino-7-hydroxynaphthalene (*loc. cit.*) forms a *diacetyl* derivative melting at 100° when it is shaken in ethereal solution with acetyl chloride and dry potassium carbonate; when it is boiled with acetic anhydride, the diacetyl derivative of 2:7-dihydroxynaphthalene is formed. C. F. B.

Ethyl Bisdiazooacetoacetate. MARIO BETTI (*Gazzetta*, 1904, 34, i, 179–194. Compare *Abstr.*, 1903, i, 78).—On hydrolysis with dilute hydrochloric or sulphuric acid, ethyl bisdiazooacetoacetate yields (1) ethylnitrosoacetoacetate, which undergoes further change into oxides of nitrogen, alcohol, carbon dioxide, acetone, acetic acid, &c., and (2) a *substance*, $CO_2Et \cdot CHAc \cdot N \cdot N \cdot NH_2$, which becomes resolved into

alcohol and isonitrosomethylpyrazolone, $NH \begin{smallmatrix} \diagup CO \cdot C \cdot N \cdot OH \\ \diagdown N = CMe \end{smallmatrix}$, which

separates in massive, yellow needles, melts and decomposes at 230°, and is soluble in alcohol or water; it is a monobasic acid, and with alkali hydroxides gives a scarlet coloration. Its *sodium* salt, $C_4H_4O_2N_3Na$, which is deposited from dilute alcohol in golden-yellow crystals, decomposes without melting at above 250° and dissolves readily in water; the aqueous solution gives coloured precipitates with salts of the heavy metals. It has the normal molecular weight in boiling alcohol. Its *benzoyl* derivative, $C_4H_4O_2N_3Bz$, crystallises from alcohol in long, silky needles melting and decomposing at 170–180°. On oxidation with nitric acid, it gives a *compound*, $NH \begin{smallmatrix} \diagup CO \cdot CH \cdot NO_2 \\ \diagdown N = CMe \end{smallmatrix}$, separating from acetic acid in shining, white crystals which melt at 276° and are

slightly soluble in ethyl or amyl alcohol or acetone. When reduced with zinc dust and dilute hydrochloric acid, it is converted into the corresponding amino-base, which, in the air, immediately becomes changed into a compound, $\begin{array}{c} \text{NH}\cdot\text{CO} \\ | \\ \text{N}:\text{CMe} \end{array} > \text{CH}\cdot\text{N}:\text{C} < \begin{array}{c} \text{CO}\text{--}\text{NH} \\ | \\ \text{CMe}:\text{N} \end{array}$, which decomposes, without melting, at above 250°.

*iso*Nitrosomethylpyrazolone may also be prepared by the action of nitrous acid on methylpyrazolone. T. H. P.

Indophthalone. CARL RENZ (*Ber.*, 1904, 37, 1221—1225).—Phthalyl chloride condenses with 2-methylindole (2 mols.) at 150—160° giving *indophthalone hydrochloride*, $\text{C}_{26}\text{H}_{20}\text{O}_2\text{N}_2\cdot\text{HCl}$, which forms a red powder, melts at 272—273°, and cannot be recrystallised; when decomposed with aqueous sodium carbonate, it gives *indophthalone*, $\text{C}_{26}\text{H}_{20}\text{O}_2\text{N}_2$, as a vermilion-coloured precipitate melting at 212°, and yielding a *potassium* derivative which crystallises in golden leaflets.

When 2-methylindole (2 mols.) is heated with phthalic anhydride in a sealed tube at 150°, the same acid, $\text{C}_9\text{H}_8\text{N}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, is formed as was obtained by Fischer (*Abstr.*, 1887, 265) in the case of molecular quantities at 100°; when, however, the mixture of the two substances (2:1) is heated in an open vessel at 185—190°, indophthalone is formed, which can be isolated as the hydrochloride (m. p. 265°). The yield in this case is small, so that it cannot be established whether the phthalone exists in two isomeric forms. W. A. D.

Constitution of the Basic Triphenylmethane Dyes. HUGO KAUFFMANN (*Zeit. Farb. Text. Chem.*, 1904, 3, 117—118).—Controversial. The author considers von Georgievics' formula (this vol., i, 351) for the triphenylmethane dyes unnecessary, the commonly accepted constitution explaining all the facts. W. A. D.

Preparation of Aromatic Substituted Guanidine from Cyanamide. ADOLF KÄMPF (*Ber.*, 1904, 37, 1681—1684).—The action of aniline hydrochloride or nitrate on cyanamide in absolute alcoholic solution leads to the formation of phenylguanidine hydrochloride or nitrate respectively. On evaporation, the hydrochloride is obtained as a yellow syrup, the nitrate in thick prisms which melt at 128°. Phenylguanidine, liberated from its hydrochloride by the action of silver oxide in aqueous solution, forms crystals which persistently retain the last traces of water and melt at 50—60°. The picrate melts at 221—222° (compare Prelinger, *Abstr.*, 1892, 950). With silver chloride, phenylguanidine forms an insoluble compound which yields phenylguanidine nitrate when acted on by nitric acid. *Dibenzoyl-phenylguanidine*, formed from the nitrate by the Schotten-Baumann method, melts at 187°, is only slightly soluble in most solvents, and on nitration yields *p*-nitrobenzoic acid. *p*-Tolylguanidine nitrate, obtained by acting with *p*-toluidine nitrate on cyanamide, melts at 146—147° and is easily soluble in alcohol, glacial acetic acid, or acetone. *p*-Tolylguanidine, precipitated as a white mass on addition of potassium hydroxide to the nitrate in aqueous solution, is easily soluble in ether.

Nitrophenylguanidines are not formed by the action of the sulphates, nitrates, or oxalates of *o*- or *p*-nitroaniline. This the author considers to be due to the complete dissociation of these salts in solution. The action of the oxalates in presence of water leads to the formation of carbamide oxalate, which melts at 170—171°.

When boiled in a reflux apparatus in absolute alcoholic solution, silver cyanamide and phenylthiocarbimide react to form the *imino-ether* of phenylcyanocarbodi-imide, $\text{NHPh}\cdot\text{C}(\text{OEt})\text{:N}\cdot\text{CN}$, which crystallises in white needles, melts at 126—127°, and is easily soluble in the ordinary solvents. With absolute alcoholic ammonia at 100° under pressure, the imino-ether yields a *substance* which melts at about 170° and has the composition $\text{C}=40\cdot12$, $\text{H}=5\cdot01$, $\text{N}=50\cdot33$ per cent. With aniline, the imino-ether yields *s*-diphenylcarbamide. G. Y.

Additive Compounds of Acids with Azo-compounds and with $\alpha\beta$ -Unsaturated Ketones at Low Temperatures. DANIEL VORLÄNDER and C. TUBANDT (*Ber.*, 1904, 37, 1644—1654. Compare Abstr., 1903, i, 495; this vol., i, 65).—Unsaturated ketones are as readily coloured by melting hydrogen bromide at -87° or by melting hydrogen chloride at -112° as by the same compounds at the ordinary temperature. Comparative experiments on the percentage of hydrogen chloride (as HCl , *A*) contained in the solid additive compounds at different temperatures have proved that the percentage is much higher at low temperatures; for example, the additive compound of dibenzylidene acetone contains 42 per cent. of hydrogen chloride at -76° , but only 22—23 at -20° or $+18^\circ$.

When, however, the hydrogen chloride combines to form the *B* compound, the velocity of addition falls with the temperature.

Azobenzene, aminoazobenzene, dimethylaminoazobenzene, acetyl- and benzoyl-aminoazobenzenes, azobenzenetrimethylammonium chloride or bromide form monohydrochlorides with characteristic orange, red, or violet-red colours. These compounds react with hydrogen chloride at -75° to -77° , yielding pale yellow-coloured polyhydrochlorides, which lose hydrogen chloride as the temperature is allowed to rise, and at 15° the highly coloured mono- or bis-hydrochlorides are formed.

Corresponding hydrobromides have been obtained: they are somewhat deeper in colour than the hydrochlorides, and the hydrogen bromide is added on more readily than the chloride, so that at 0° or -20° polyhydrobromides are obtained.

The hydrobromide *B* of dibenzylideneacetone is more readily formed by the action of hydrogen bromide on the ketone itself than on the hydrobromide *A* at the same temperature.

Benzylideneacetophenone hydrobromide *B* melts at about 110° , and when crystallised from warm glacial acetic acid is decomposed into its components.

The following general conclusions are drawn:

(1) The additive reactions between acids and unsaturated compounds (amines, ketones, esters, salts, &c.) are quite different from processes of neutralisation of an acid by a base with elimination of water.

(2) Opposed to the addition is a process of dissociation into acid and

the unsaturated compound. This is often confused, when it occurs in aqueous or alcoholic solution, with hydrolysis or alcoholysis.

(3) The addition and dissociation are dependent on the composition of the components, on any third substance which may be present, on temperature, pressure, light, &c.

(4) A component is capable of displacing another from an additive compound, but the reaction is much slower than when the two components combine directly.

(5) The same unsaturated compound can give rise to isomeric additive products with the same acid. This phenomenon is termed additive isomerism, and cannot be explained by the ordinary theories of valency or ionisation.

J. J. S.

Solid Solutions and Isomorphism. GIUSEPPE BRUNI (*Gazzetta*, 1904, 34, i, 144—146. Compare Bruni and Gorni, *Abstr.*, 1899, ii, 731; 1900, ii, 714; and Garelli and Calzolari, *Abstr.*, 1899, ii, 732). —[With BILLOWS.]—*p*-Azotoluene crystallises in the monoclinic system [$a:b:c=0.5687:1:1.7105$; $\beta=89^{\circ}44'$]. *p*-Hydrazotoluene also forms monoclinic crystals [$a:b:c=0.6279:1:2.0286$; $\beta=89^{\circ}49'$].

T. H. P.

The so-called Diazosulphonaphtholsulphonic Acids of the German Patent 121226. HANS BUCHERER (*Zeit. Farb. Text. Chem.*, 1904, 3, 118—120).—The compounds obtained by the action of sulphites on diazotised β -naphthylamine-5:7- and -8:6-disulphonic acids are apparently neither dihydroxyazonaphthalenedisulphonic acids nor diazosulphonaphtholsulphonic acids (compare Hantzsch, *Abstr.*, 1897, i, 185); they do not possess the tinctorial qualities of the former, neither are they reducible, like the latter substances, to hydroxynaphthylhydrazinesulphonic acids or the naphthylaminesulphonic acids from which they are derived. Their nature remains to be more fully investigated.

W. A. D.

Electrolytic Preparation of Azo-dyes. WALTHER LÖB (*Zeit. Elektrochem.*, 1904, 10, 237—238).—When a solution containing an aromatic amine and sodium nitrite is electrolysed with a platinum anode, it is probable that a diazo-compound is formed. It is not possible, however, to isolate it. When a phenol is added to the solution, it combines with the diazo-compound before it can be changed in any other way, and the corresponding dye is produced. The materials are used in molecular proportions, the phenol being preferably in a soluble form and the anode compartment in which the reaction occurs is separated from the cathode by a porous diaphragm. From 0.005 to 0.06 ampere per sq. cm. may be used, and it is unnecessary to cool the solutions below the ordinary temperature.

T. E.

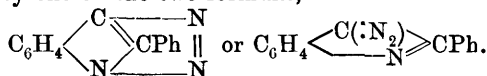
[Azo-dyes from 1-Chloro-2:6-diaminobenzene-4-sulphonic Acid.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 150373).—1-Chloro-2:6-diaminobenzene-4-sulphonic acid, prepared by reducing chlorodinitrobenzenesulphonic acid (D.R.-P. 116759) with tin and

hydrochloric acid, forms colourless needles containing H_2O , insoluble in water, soluble in dilute alkalis, and reprecipitated by acids. Nitrous acid forms a yellow tetrazo-compound, which combines with naphthols and their sulphonic acids to form azo-dyes, which are free from chlorine and are identical with those prepared from diaminophenol-sulphonic acid. The chlorine atom has therefore been replaced by the hydroxyl group. C. H. D.

Azo-dye from 4-Acetyl-2:4-diaminophenol-6-sulphonic Acid. LEOPOLD CASSELLA & Co. (D.R.-P. 149106).—4-Acetyl-2:4-diaminophenol-6-sulphonic acid, prepared from acetyl-*p*-aminophenol by sulphonation, nitration, and reduction, yields a soluble, yellow diazonium compound, which combines with β -naphthol to form a claret-coloured dye, which becomes black on subsequent treatment with an alkali chromate. C. H. D.

Diazoamino-compounds of Aminonaphtholsulphonic Acids. LUDWIG PAUL (*Zeit. angew. Chem.*, 1904, 17, 363—365).—When the tetrazo-derivative of tolidine is added to an aqueous solution of aminonaphtholdisulphonic acid-H, a slight precipitate is formed if the latter acid contains some monosulphonic acid. The filtrate contains a diazo-amino-compound, and addition of *p*-nitrodiazobenzene causes a voluminous, bluish-red precipitate, which, when introduced in the pasty condition into a concentrated solution of sodium salicylate or of sodium phenoxide, forms the monoazo-dye of *p*-nitrodiazobenzene and aminonaphtholdisulphonic acid-H on the one hand, and the intermediate compound of tetrazoditolyl and phenol (or salicylic acid) on the other. When the precipitate, however, is well washed with water, it is transformed into the bluish-green aminoazo-compound. The sodium salt of aminonaphtholsulphonic acid- γ in combination with tetrazoditolyl also forms a diazoamino-compound which interacts with *p*-nitrodiazobenzene. When molecular amounts of tetrazoditolyl and sodium β -naphtholdisulphonate- γ are united in moderately dilute aqueous solution, flesh-coloured leaflets quickly separate, which alkali changes into a red compound. The intermediate compound is converted by sodium hydrogen sulphite into a substance which is not a dye. A. McK.

Diazoindoles. ANGELO ANGELI and ANTONINO D'ANGELO (*Atti R. Accad. Lincei*, 1904, [v], 13, i, 258—259).—3-Amino-2-phenylindole, on treatment with nitrous acid, is converted into a substance, $\text{C}_{14}\text{H}_9\text{N}_3$, which crystallises from light petroleum in orange-yellow prisms, melts at 115° , and appears to be the anhydride of a diazo-hydroxide, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}(\text{N}_2\cdot\text{OH}) \\ \text{NH} \end{smallmatrix} \gg \text{CPh}$. The structure would thus be represented by one of the two formulæ,



W. A. D.

[Azo-compounds of Phenylmethylpyrazolone.] FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 150125).—A yellow azo-compound, capable of forming metallic lakes, is obtained by combining diazotised *o*-amino-*p*-sulphobenzoic acid with phenylmethylpyrazolone.
C. H. D.

Diazo-derivatives of Proteids. Z. TREVES and A. PELLIZZA (*Atti R. Accad. Sci. Torino*, 1904, 39, 429—434).—When commercial casein, freed from fat, is treated with nitrous acid in the usual manner of diazotisation, a yellow product is formed which is decomposed by light, alkali hydroxides, or warm concentrated acids in presence of cuprous chloride, with evolution of nitrogen; the yellow mass couples with alkaline β -naphthol, salicylic acid, or amines to form brownish-red azo-compounds. Blood albumin, fibrin, and fish glue show the same behaviour under similar conditions. Fibrin and casein which have been exposed to formaldehyde can still be diazotised, but more slowly, and the product is insoluble in alkali hydroxides. The ordinary diazo-derivatives give the biuret reaction, but when they are obtained from proteid which has been treated with formaldehyde, this is no longer the case. The mode of formation of the diazo-compounds is discussed.
W. A. D.

Formation of Hydrogen Cyanide by the Oxidation of Proteids. R. H. ADERS PLIMMER (*J. Physiol.*, 1904, 31, 65—80).—By the oxidation of proteids with Neumann's acid mixture, hydrogen cyanide is evolved; the amount for each proteid is constant whether it has been hydrolysed or not. The amount varies with different proteids. The amino-acids yield only a small quantity. Oxidation with potassium dichromate and sulphuric acid gives rise to the same amount of the acid, but the yield is small when oxidation is carried out with concentrated sulphuric acid, sulphuric acid and manganese dioxide, or sulphuric acid and potassium permanganate.
W. D. H.

Nucleo-proteids and their Decomposition Products. CARLO FOÀ (*Atti R. Accad. Lincei*, 1904, 13, i, 342—349).—The author's experiments show that the nucleo-proteid of Bang (*Abstr.*, 1900, i, 57) and also that of Huiskamp (*Abstr.*, 1900, ii, 461) are decomposed, by digestion with hydrochloric acid, into an insoluble residue of nuclein, and a proteid substance which remains dissolved in the hydrochloric acid and presents all the reactions of histon. It is not possible to distinguish a nucleo proteid from a nucleo-histon by the presence in the latter, and the absence from the former, of histon. These two groups of substances should therefore be classed together.
T. H. P.

Hydrolysis of Casein. ZDENKO H. SKRAUP (*Ber.*, 1904, 37, 1596—1597).—A number of new products of hydrolysis have been prepared in crystalline form by an improved method to be described later.

Diaminoglutaric acid forms prisms and melts at 238°, *diaminoadipic*

acid also forms prisms and melts at about 270° . Both acids form soluble, crystalline *copper* salts. Diamino-derivatives of dibasic acids have not hitherto been detected amongst the products of the hydrolysis of proteids.

Many aminohydroxy-acids have been found. *Aminohydroxysuccinic acid* melts at 320° . An *acid*, $C_8H_{16}O_5N_2$, crystallises well and melts at 243° , and is possibly a diaminodihydroxysuberlic acid.

Caseanic acid, $C_9H_{16}O_7N_2$, forms very sparingly soluble, characteristic crystals, melts at 192° , and forms an insoluble, bluish-green *copper* salt. The *hydrochloride* crystallises in tablets or long prisms. The acid is tribasic and probably contains one hydroxyl group. *Caseic acid*, $C_{12}H_{16}O_5N_2$, forms a *dextrorotatory* modification crystallising in prisms and melting at 226° , and an *inactive* modification melting at 246° . Both forms yield the same violet *copper* salt and the same *hydrochloride*.
C. H. D.

Decomposition Products of Elastin. EMIL ABDERHALDEN and ALFRED SCHITTENHELM (*Zeit. physiol. Chem.*, 1904, 41, 293—298. Compare Horbaczewski, *Abstr.*, 1883, 927; 1886, 270; Schwarz, 1894, ii, 146; Bergh, 1898, i, 608; Hedin, *ibid.*, 608; Kossel and Kutscher, *ibid.*, i, 718).—The following products have been isolated from elastin after hydrolysis with concentrated hydrochloric acid: glycine, 25.75; leucine, 21.38; alanine, 6.58; phenylalanine, 3.89; pyrrolidine-2-carboxylic acid, 1.74; glutamic acid, 0.76; and amino-valeric acid, 1.0 per cent.
J. J. S.

Pigment of the Suprarenal Capsules. C. GESSARD (*Compt. rend.*, 1904, 138, 586—588). GABRIEL BERTRAND (*ibid.*, 649—650).—The chromogen of this pigment is regarded as the product of the action of tyrosinase on tyrosine. In the second paper, this conclusion is commented on adversely.
W. D. H.

Colour Reactions; the Result of the Action of Tyrosinase. C. GESSARD (*Compt. rend.*, 1904, 138, 774—775. Compare *Abstr.*, 1902, i, 196; 1903, ii, 165).—The action of tyrosinase on tyrosine presents two distinct phases; first a rose-red, then a violet coloration, followed by precipitation of the coloured product. The first phase alone is attributed to ferment action. The chemical nature of the coloured products is as yet undetermined.
W. D. H.

Decomposition of Yeast Nucleic Acid by Bacteria. IV. ALFRED SCHITTENHELM and F. SCHRÖTER (*Zeit. physiol. Chem.*, 1904, 41, 284—292. Compare *Abstr.*, 1903, ii, 679, and this vol., ii, 139).—Among the products obtained by the action of a pure culture of *Bacterium coli* on sodium yeast-nucleate are phosphoric acid, carbon dioxide, formic and oxalic acids, ammonia, alcohol, xanthine, and hypoxanthine. Acetic acid, guanine, and adenine could not be isolated. Probably cytosine and uracil are formed. An acid melting at 183° has also been isolated.
J. J. S.

Decomposition Products of Thymus-histon. EMIL ABDERHALDEN and PETER RONA (*Zeit. physiol. Chem.*, 1904, 41, 278—283. Compare Kossel and Kutscher, *ibid.*, 1900, 31, 188).—Thymus-histon was hydrolysed with concentrated hydrochloric acid and the products examined by Fischer's esterification method. Among the products isolated were glycine, 0.5; alanine, 3.46; leucine, 11.8; pyrrolidine-2-carboxylic acid, 1.46; phenylalanine, 2.2; glutamic acid, 0.53 per cent. Tyrosine (5.2 per cent.) was also isolated, and indications of the presence of aspartic acid and of cystine were obtained. J. J. S.

Adrenaline [Epinephrine]. II. HERMANN PAULY (*Ber.*, 1904, 37, 1388—1401. Compare this vol., i, 128; also Abel, *Abstr.*, 1903, i, 376, 784, and this vol., i, 264, and Jowett, *Trans.*, 1904, 85, 192).—In reply to Abel, experiments have been made to prove that the adrenaline analysed was (a) free from organic phosphorus compounds, (b) free from adhering ammonia, (c) free from water of crystallisation. The formula $C_9H_{13}O_3N$ is retained.

Adrenaline urate, $C_9H_{13}O_3N \cdot C_5H_4O_3N_4$, has been obtained in the form of small, pointed plates. A *dibenzoyl* (?) derivative, $C_9H_{11}O_3NBz_2$, sintering at 70° and melting at 90° has been obtained; it gives the typical catechol reaction. The following constitution is suggested: $C_6H_3(OH)_2 \cdot CH(NHMe) \cdot CH_2 \cdot OH$ [$CH : (OH)_2 = 1 : 3 : 4$]. J. J. S.

Organic Colloids from Town Sewage. WILHELM BILTZ and OTTO KRÖHNKE (*Ber.*, 1904, 37, 1745—1754. Compare Biltz, this vol., ii, 324).—The organic substances in sewage are mostly in solution as colloids. On dialysis, the inorganic constituents rapidly vanish, but about one-half or one-third of the organic constituent cannot be dialysed. On passing an electric current, the amount of oxidisable substance at the anode increases, whilst that at the cathode decreases, showing that the putrefactive matter in sewage is charged negatively relatively to water. This is precipitated by positively charged colloids such as iron or zirconium hydroxides. The authors extend their results to explain the theory of the bacterial method of treating sewage. E. F. A.

Enzyme Actions considered as Equilibria in a Homogeneous System. ARIE W. VISSER (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 6, 605—609).—From his experiments, the author concludes that sucrose may be regenerated to a slight extent from dextrose and lævulose by means of invertase. Further, salicin may be regenerated from saligenin and dextrose by means of emulsin. Invertase and emulsin retain their quantitative activity for some weeks in sterilised solutions. The average factor for the change of velocity of the sucrose decomposition = 2 for 10° between 0° and 25°. By a change of temperature from 0° to 25°, the equilibrium is displaced very little, or not at all. At a definite temperature, the change in concentration of the enzymes has no influence on the equilibrium, but only on the velocity. The intensity of the invertase is smaller in proportion as the quantity of invert sugar present with

the same amount of sucrose is greater. The intensity depends not only on the quantity of invert sugar, but also on the quantity of sucrose present in the solution; it is smaller when this quantity is greater. The reversible enzyme actions observed proceed very slowly.

A. McK.

Influence of Acidity on Enzymes. PAUL PETIT (*Compt. rend.*, 1904, 138, 1003—1004).—It is generally admitted that barley contains an enzyme which saccharifies, but does not liquefy, starch paste, the liquefying action being only developed on germination; the author, however, finds that the same effect is produced by simply varying the acidity. Infusions of barley flour made with distilled water, or with solutions containing 0.2, 0.49, 0.98 grams of lactic acid per litre, were examined in respect of their action on starch paste; the first saccharified, but did not liquefy, the paste; the first two acid solutions both liquefied and saccharified, whilst the third did not liquefy, and only saccharified to a slight extent. Further experiments on the influence of traces of alkali on the action of infusions of barley served to show that the enzyme forms a compound with the alkali which is broken down by acids without the enzyme suffering any change, and the conclusion is drawn that the saccharifying enzyme in barley is in a state of combination which is destroyed by acids, and that a variation in the acidity confers the power of liquefying on the enzyme, independently of germination.

M. A. W.

Probable Constitution of the Diastase of Rennet. ALBERTO SCALA (*Chem. Centr.*, 1904, i, 1019; from *Staz. sperim. agrar. ital.*, 36, 941—944).—The author has arrived at the following conclusions: (1) phosphoric acid is not combined with the diastase of rennet in the form of an ester, but is attached to the amino-groups forming a simple salt. (2) The mercury compound is a true substitution product, the mercury taking the place of hydrogen atoms of the amino-groups. (3) The diastase is an albumose. (4) The diastases and their mercury compounds are oxidised by distilled water, drinking-water containing earthy carbonates, and all oxidising agents. By slight oxidation, the lateral amino-groups are split off as ammonia, whilst by the action of potassium permanganate ammonia and nitrous acid are formed. (5) The activity of the diastases depends on the presence of the amino-groups; when all these groups contain mercury, the compound has no longer the power of coagulating milk, but when only a portion of the groups contain mercury, the compound retains this power. (6) Acids and mercury render the diastases less liable to oxidation, although they do not completely prevent it.

E. W. W.

Action of Formaldehyde on the Diastatic Force of Malt. KARL J. SOMLÓ and ALADÁR VON LÁSZLÓFFY (*Chem. Centr.*, 1904, i, 1365; from *Oesterr. Chem. Zeit.*, 7, 126—128).—Experiments on the action of various antiseptics on green malt have shown that most of these substances have an injurious effect on the diastase. In some cases, however, it has been found possible to prevent this action by modifying the conditions with reference to time and the method of

action. In all cases, it is, of course, necessary to completely wash out the antiseptic before testing the activity of the malt. The action of the diastase of a green malt was found to be considerably increased by treating it with a 2 or 5 per cent. solution of formaldehyde for a time varying from 20 minutes to 4 hours. Immersion of the malt in a 2 per cent. solution of commercial formaldehyde for 2 hours was sufficient to cause a pure fermentation. The hypothesis of the formation of starch from formaldehyde on the green plant possibly finds some confirmation in these facts.

E. W. W.

The Function of Peroxides in the Living Cell. VIII. Peroxydases. ALEXIS BACH and ROBERT CHODAT (*Ber.*, 1904, 37, 1342—1348. Compare *Abstr.*, 1902, ii, 344, 522; 1903, i, 377, 378, 671; this vol., i, 359).—Preparations of peroxydase from horse-radish are free from oxygenase, catalase, amylase, invertase, emulsin, and proteolytic enzymes. The action of peroxydase is more easily studied quantitatively than that of a hydrolytic enzyme, from the fact that the quantities of all the substances taking part in the reaction can be measured. Pyrogallol is not attacked by either hydrogen peroxide or peroxydase separately, and since the product of the reaction, purpurogallin, is insoluble, the reaction proceeds completely in one direction. With constant quantities of hydrogen peroxide and pyrogallol, the purpurogallin formed is proportional to the peroxydase added, and with constant peroxydase and pyrogallol the purpurogallin is proportional to the hydrogen peroxide added. The concentration of the pyrogallol is without influence. Peroxydase thus reacts with hydrogen peroxide in a constant proportion, and must probably be considered as forming a definite compound with it. When equivalent solutions of peroxydase and hydrogen peroxide are mixed, both compounds disappear within 24 hours without evolution of oxygen.

C. H. D.

Yeast Catalase. NEUMANN WENDER (*Chem. Zeit.*, 1904, 28, 300—301, 322—323).—Since Omelianski has shown (this vol., ii, 277) that the decomposition of formic acid into hydrogen and carbon dioxide by means of *Bacillus formicicum* is not due to an enzyme, but is occasioned by the living plasma, the author has studied the decomposition of hydrogen peroxide by yeast catalase, and concludes from his experiments that the catalytic decomposition observed is enzymatic. Various specimens of yeast were taken and the amount of oxygen evolved from hydrogen peroxide under the influence of a given weight of yeast in a given time was determined. Dead yeast, prepared by the alcohol-ether method of Albert, or by the acetone method of Rapp, could still induce the catalytic decomposition of hydrogen peroxide.

The influence of temperature on the catalysis was studied. There was no diminution in activity when the yeast was heated for one hour at temperatures ranging from 10° to 50°; at 60°, the yeast lost considerably in activity, and at 70° it lost its power entirely. More exact determinations showed that the temperature at which yeast ceased to be active was 68—72°, and approximated to that at which melibiase and invertase lose their specific properties.

The catalytic action of zymase on hydrogen peroxide was also

examined. Bottom yeast, when kept for some time at 45—50°, lost entirely its power of inducing alcoholic fermentation, but the catalytic action on hydrogen peroxide was quite as marked as it was before the temperature was raised. Further, yeast in which the maltase had been destroyed, still possessed its catalytic power. During the catalysis of hydrogen peroxide by yeast, the zymase in the latter diminishes slightly in activity. The volume of oxygen obtained by the action of yeast on hydrogen peroxide in the presence of definite amounts of acetic, oxalic, tartaric, lactic, sulphuric, and hydrochloric acids, sodium carbonate, sodium hydroxide, silver nitrate, mercuric chloride, alcohol, ether, and potassium thiocyanate respectively was measured. Yeast catalase was shown to be remarkably stable towards the substances just enumerated.

Yeast catalase, in the dry condition, can be heated at 100° without losing its activity.

A. McK.

Fermentation Experiments with Extract from Top-fermentation Yeast. ARTHUR HARDEN and WILLIAM JOHN YOUNG (*Ber.*, 1904, 37, 1052—1070).—With sucrose and with dextrose the sugar-fermentation by the extract was practically identical, but in each case was far less than with Buchner's extract from bottom-yeast. The self-fermentation of the extract was very variable, ranging from 0.02 to 0.32 gram of carbon dioxide per 25 c.c. of extract; in absolute measure it corresponds closely with the figures given by Buchner for bottom-yeast (0.10 to 0.459), and by Macfadyen, Morris, and Rowland for top-yeast (0.06 to 0.4959, *Abstr.*, 1901, i, 59). As the fermentation of added sugar proceeds only slowly as compared with that produced by Buchner's extract, the self-fermentation represents a considerable proportion of the total in these cases. It is also noticeable that the fermentation, although much smaller in extent, is proportionately much more rapid than that produced by Buchner's extract; the total fermentation was seldom greater than 1.5 times that in the first 24 hours, whilst Buchner found a ratio ranging from 1.5 to 3.0; this is probably due to the presence of a smaller proportion of zymase or a difference in the proportion of proteolytic enzyme.

No difference was observed in a series of experiments in which kieselguhr was not used in preparing the extract, which was obtained simply by the action of sand.

The fermentation of pure yeast-glycogen by the extract proceeds to a much smaller extent than when an equivalent quantity of dextrose is added to the extract; the yield of carbon dioxide is, however, in all cases considerably greater in presence of glycogen than in the self-fermentation of the simple extract.

Both when the extract is allowed to ferment by itself, and when dextrose is added, the weights of alcohol and carbon dioxide produced are approximately equal, the theoretical ratio is 1.04, and the values found were 0.90, 1.12, 0.95, 0.91, and 0.92; similar results were obtained by Buchner, whilst Macfadyen, Morris, and Rowland obtained similar results only with very energetic fermentation.

Dilution of the extract with water produces no appreciable effect on the self-fermentation, but in presence of dextrose, dilution with

3 volumes of water reduces the yield of carbon dioxide to 0.5 or 0.7 of that with undiluted extract; dilution with sugar-solution, on the other hand, produces little or no effect. This differs from Macfadyen, Morris, and Rowland's results, who concluded that dilution with one or two volumes of water stopped both the self-fermentation and the sugar-fermentation, but agrees with Buchner's results, who did not study the self-fermentation, but found that dilution slightly reduced the sugar-fermentation.

In agreement with the observations both of Macfadyen, Morris, and Rowland, and of Buchner, the weight of sugar removed from the solution was always greater than that calculated from the weight of carbon dioxide and alcohol produced. The sugar appears, however, not to be decomposed, but converted into a form which is not reducible as such, but becomes reducible again when hydrolysed by acids. As dextrose is decomposed by acids, it was necessary to make a correction for this decomposition before trustworthy results could be obtained; the correction was determined by experiments with pure dextrose, and was found to be proportional to the total weight of dextrose, both in $N/2$ and in $3N$ -acid solutions. Whether the non-reducible product is of the nature of a carbohydrate could not be determined, as all attempts to isolate it were unsuccessful. It is apparently produced not by xymase, but by some different enzyme, since the weight of sugar changed in this way is very much the same in solutions which undergo a large, and those which undergo only a slight, fermentation.

T. M. L.

Preparation of Organo-lead and Mercury Compounds.
PAUL PFEIFFER and P. TRUSKIER (*Ber.*, 1904, 37, 1125—1127).—Lead tetraphenyl (compare Polis, *Abstr.*, 1888, 283) is readily obtained by the action of lead chloride on an ethereal solution of magnesium phenyl bromide. Lead triethyl iodide may be obtained from lead chloride and magnesium ethyl iodide. Mercury diphenyl melting at 120° may be obtained by a similar method.

J. J. S.

Organic Chemistry.

Electrolytic Preparation of Chloroform from Acetone. JOHN E. TEEPLE (*J. Amer. Chem. Soc.*, 1904, 26, 536—543. Compare this vol., i, 362).—When a solution of sodium or potassium chloride containing acetone is electrolysed, chloroform is produced. Sodium hypochlorite is formed from the action of the chlorine liberated at the anode, on the sodium hydroxide formed at the cathode; the sodium hypochlorite then acts on the acetone. The solution should be only feebly, if at all, alkaline, the temperature is kept below 25°, whilst a high current density is employed at the cathode and a comparatively low one at the anode.

The course of the electrolysis was followed by determining the amount of chloroform produced after definite times and by titrating the alkali produced with trinitrobenzene as indicator; it was shown how the yield of chloroform is diminished if the alkali is allowed to accumulate.

A. McK.

Differentiation between Primary, Secondary, and Tertiary Alcohols of the Fatty Series. ANDRÉ KLING and MARCEL VIARD (*Compt. rend.*, 1172—1173).—The method is based on the behaviour of the three classes of alcohols on being heated. At the temperature of boiling naphthalene (218°) tertiary alcohols are dehydrated, whilst primary and secondary derivatives remain intact. At a still higher temperature, the boiling point of anthracene (360°), both tertiary and secondary alcohols are decomposed; the primary compounds alone remain unacted on. To determine whether an alcohol is primary, secondary, or tertiary, it is only necessary to measure the vapour density at 218° and 360°; Victor Meyer's method may be conveniently used. It is shown that the method is applicable to all primary alcohols up to those containing seven carbon atoms, to secondary alcohols as far as derivatives of nine carbon atoms, and to tertiary alcohols with twelve carbon atoms. Aromatic and unsaturated alcohols do not give satisfactory results.

S. S.

Alkyloxides. JULIUS W. BRÜHL (*Ber.*, 1904, 37, 2066—2068. Compare Brühl and Biltz, *Abstr.*, 1891, 656).—Metallic sodium is finely divided under boiling xylene (*Ber.*, 1902, 35, 3516), and a further quantity of dry xylene is added so that there are 250 c.c. of liquid for each gram-molecule of sodium. The theoretical amount of methyl alcohol dissolved in twice its volume of dry xylene is run in, whilst the mixture is kept cool and well stirred by aid of the apparatus recently described (this vol., ii, 248). The reaction is completed by gently warming, and should not take more than a few hours. The sodium methoxide obtained as a snow-white, flocculent mass suspended in the xylene, is free from methyl alcohol, and is extremely active. Other alkyloxides may be prepared in a similar manner. Sodium amyloxide is soluble in benzene.

J. J. S.

Synthetical *iso*Amyl Alcohol and the Amyl Alcohol of Commerce. RENÉ LOCQUIN (*Bull. Soc. chim.*, 1904, [iii], 31, 599—601).—*iso*Amyl alcohol, prepared by Grignard and Tissier's method from *isobutyl* chloride and trioxymethylene, boils at 131° (corr.) under 765 mm. pressure, has a sp. gr. 0·823 at 0°/4°, furnishes an iodide boiling at 147° (corr.) under 765 mm. pressure, and a phenylurethane which melts at 54° (compare Hofmann, *Annalen*, 1850, 74, 16). The iodide prepared from ordinary amyl alcohol boils at 144—150° and the crude phenylurethane from this source melts at 40° and, owing to its ready solubility, is difficult to purify. The author considers that in view of these differences care should be taken, in describing amyl derivatives obtained from ordinary amyl alcohol, to specify the nature of the amyl radicle.

T. A. H.

Dichloromethyl Oxide. MARCEL DESCUDÉ (*Compt. rend.*, 1904, 138, 1110—1112. Compare Abstr., 1901, i, 504, 644; 1902, i, 339, 738).—Trioxymethylene reacts with phosphorus trichloride in the presence of a small quantity of fused zinc chloride to form dichloromethyl oxide boiling at 102—105° under the ordinary pressure, and the yield is equal to the weight of trioxymethylene taken. The product of the action of phosphorus trichloride on a 40 per cent. solution of formaldehyde is the same as that obtained by the action of hydrogen chloride on a concentrated solution of formaldehyde (compare Littrescheid, Abstr., 1901, i, 443, and Coops, Abstr., 1902, i, 77); it has the composition 4CH₂O, 3HCl, and the probable constitution is represented by the formula

$$\text{CH}_2 \begin{array}{c} \text{O} \cdot \text{CH}_2 \text{---} \text{OHCl} \\ \text{OHCl} \cdot \text{CH}_2 \cdot \text{OHCl} \end{array} \text{CH}_2.$$

M. A. W.

Application of the Grignard Reaction to the Halogen Ethers of Tertiary Alcohols. LOUIS BOUVEAULT (*Compt. rend.*, 1904, 138, 1108—1110).—*tert.*-Amyl and -butyl chlorides form additive compounds with magnesium at temperatures between 5° and 15°; at higher temperatures, a secondary reaction takes place with the formation of the corresponding paraffin and olefine. These magnesium derivatives react normally with carbon dioxide, magnesium *tert.*-butyl chloride giving a yield of 30 per cent. of pivalic acid, and magnesium *tert.*-amyl chloride a yield of 60 per cent. of *aa*-dimethylbutyric acid. Magnesium *tert.*-butyl chloride reacts with methyl formate to form *tert.*-butylcarbinol and a small quantity of the corresponding aldehyde; and with dimethylformamide to yield a small quantity of an aldehyde not yet identified, the semicarbazone of which melts at 192°; magnesium *tert.*-amyl chloride reacts with diethylformamide to give *β-iso*amylene (trimethylethylene) and a basic substance, C₁₀H₂₃N, probably CMe₂Et·CH₂·NEt₂, boiling at 165—166°, or at 52° under 10 mm. pressure.

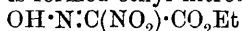
M. A. W.

***iso*Nitrosoacetic Esters.** LOUIS BOUVEAULT and ANDRÉ WAHL (*Bull. Soc. chim.*, 1904, [iii], 31, 675—679. Compare Bouveault and Locquin, Abstr., 1902, i, 704 and 705).—When nitrosylsulphuric acid is added to ethyl acetate, a vigorous reaction ensues, which, when

moderated by previous solution of the reacting substances in sulphuric acid and cooling to -10° , gives rise to the formation of acetic acid and ethyl isonitrosoacetate, $\text{OH}\cdot\text{N}\cdot\text{C}\cdot\text{H}\cdot\text{CO}_2\text{Et}$. The latter crystallises in long, white needles from ether on addition of light petroleum, melts at 35° , and boils at $110-115^{\circ}$ under 15 mm. pressure (compare Cramer, Abstr., 1892, i, 699). The free acid crystallises in prisms, melts at $143-144^{\circ}$, and dissolves in aqueous solutions of the alkali hydroxides with a yellow colour. The *methyl* ester, similarly prepared, crystallises in fine prisms, melts at 55° , boils at 100° under 15 mm. pressure, and is very soluble in water; the *isobutyl* ester is a slightly coloured, viscid liquid which distils at $117-118^{\circ}$ under 10 mm. pressure, has a sp. gr. $1\cdot082$ at $0^{\circ}/4^{\circ}$, and is insoluble in water, but dissolves in alkaline liquids with a yellow colour.

The authors consider that in the formation of these substances an isonitrosoacetoacetic ester is first formed and that this subsequently undergoes hydrolysis, forming acetic acid and the isonitrosoacetic ester. The fact that ethyl isonitrosoacetoacetate, dissolved in sulphuric acid, can be recovered without the formation of ethyl isonitrosoacetate is, however, not in harmony with this hypothesis. T. A. H.

Action of Nitrogen Trioxide and Peroxide on Nitrosoacetic Esters. LOUIS BOUVEAULT and ANDRÉ WAHL (*Bull. Soc. chim.*, 1904, [iii], 31, 679—682. Compare Abstr., 1903, i, 677, and preceding abstract).—When ethyl isonitrosoacetate is treated with nitrogen peroxide, there is formed ethyl nitroisonitrosoacetate,



(Jovitschitsch, Abstr., 1898, i, 64, and 1902, i, 202), and, as the result of the partial decomposition of this, ethyl bisanhydronitroacetate, $\text{C}_2(\text{NO})_2(\text{CO}_2\text{Et})_2$.

When a current of nitrogen trioxide is passed through *isobutyl* isonitrosoacetate, the temperature being maintained below $30-35^{\circ}$, and the resulting *isobutyl* oximinonitroacetate is distilled, a violent decomposition ensues. This may be moderated by previous solution of the reaction product in *isobutyl* alcohol, and when such a solution is distilled *isobutyl glyoxalate* and *isobutyl bisanhydronitroacetate* are produced. The former is a pungent, mobile, yellow liquid, which boils at $75-80^{\circ}$ under 15 mm. pressure, readily combines with water, and reduces an ammoniacal solution of silver oxide in the cold; the corresponding *semicarbazone* forms white leaflets and melts at $214-215^{\circ}$. *isoButyl* bisanhydronitroacetate, $\text{C}_2(\text{NO})_2(\text{CO}_2\cdot\text{C}_4\text{H}_9)_2$, is a viscid, yellow liquid which boils at $180-185^{\circ}$ under 15 mm. pressure, has sp. gr. $1\cdot156$ at $0^{\circ}/4^{\circ}$, and is insoluble in water.

Corresponding products are obtained when ethyl isonitrosoacetate is similarly treated. T. A. H.

Pentenoic and Hexenoic Acids. FRITZ FICHTER and ALFRED PRISTER (*Ber.*, 1904, 37, 1997—2001).—The following improvements have been made in Fittig and Spenser's method (Abstr., 1895, i, 204) of preparing Δ^{β} -pentenoic acid. Ethyl acetylsuccinate is prepared by means of ethyl bromoacetate, and is reduced by aluminium amalgam to ethyl methylparaconate, which boils at 156° under 17 mm. pressure;

the ester is hydrolysed to its acid by an excess of aqueous barium hydroxide.

Δ^{α} -Hexenoic acid is best prepared by heating ethyl α -bromohexanoate with quinoline at 185° ; the product is a mixture of ethyl Δ^{α} -hexenoate with a small quantity of the isomeric Δ^{β} -hexenoate and is hydrolysed to the corresponding acids, which are then separated by Fittig's method. $\Delta\gamma$ -Hexenoic acid is oxidised by cold aqueous potassium permanganate to acetic acid and succinic acid.

Δ^{δ} -Hexenoic acid (compare Wallach, Abstr., 1900, i, 590) boils at 203° , has a sp. gr. 0.9639 at 19.2° , n_D 1.4375 at 19.1° , and a mol. refraction 31.02.

The hexenoic acids are best characterised by their *p*-toluidides, which are purified by distillation under reduced pressure.

Δ^{α} -Penteno-*p*-toluidide boils at 230 — 235° under 20 mm. pressure, and crystallises from 50 per cent. acetic acid in long clusters of needles melting at 110° . Δ^{β} -Penteno-*p*-toluidide crystallises from hot water in lustrous leaflets and melts at 106° . $\Delta\gamma$ -Penteno-*p*-toluidide boils at 205° under 16 mm. pressure, separates from light petroleum in lustrous needles, and melts at 81.5° . The *p*-toluidide from Δ^{α} -hexenoic acid boils at 205 — 215° under 13 mm. pressure, crystallises from benzene in slender needles, and melts at 125° ; that from Δ^{β} -hexenoic acid crystallises from light petroleum in leaflets melting at 95.5° , whilst that derived from $\Delta\gamma$ -hexenoic acid boils at 200 — 205° under 12 mm. pressure and melts at 103° . Δ^{δ} -Hexeno-*p*-toluidide boils at 220° under 14 mm. pressure and crystallises from light petroleum in needles melting at 75° .

o-Nitro- Δ^{α} -hexeno-*p*-toluidide, prepared by nitrating the *p*-toluidide of Δ^{α} -hexenoic acid, crystallises from alcohol in slender, yellow needles and melts at 87° .

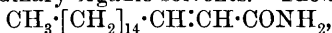
Phenylisocrotonic anhydride, $C_{20}H_{18}O_3$, obtained by the action of phosphorus oxychloride on sodium phenylisocrotonate (2 mols.), crystallises from benzene in white leaflets, melts at 120 — 121° , and combines with aniline to form phenylisocrotonanilide, $C_{16}H_{15}ON$, which crystallises from a mixture of benzene and light petroleum in spangles and melts at 89 — 90° . Phenylisocrotono-*p*-toluidide forms white leaflets and melts at 149° .

W. A. D.

New Acids of the Oleic Series. I. Δ^{β} -Oleic Acid. GIACOMO PONZIO (*Atti R. Accad. Sci. Torino*, 1903—1904, 39, 552—560).— α -Iodostearic acid, $CH_3 \cdot [CH_2]_{15} \cdot CHI \cdot CO_2H$, prepared by the action of alcoholic potassium iodide on α -bromostearic acid, crystallises from alcohol or light petroleum in shining, white plates melting at 66° ; it is stable towards light and dissolves in the ordinary organic solvents.

Δ^{β} -Oleic acid, $CH_3 \cdot [CH_2]_{14} \cdot CH : CH \cdot CO_2H$, obtained, together with α -hydroxystearic acid, by the action of alcoholic potassium hydroxide on α -iodostearic acid, crystallises from alcohol in broad plates or slender, white needles, melts at 59° , and resolidifies at 52° ; it is stable in the air and is moderately soluble in light petroleum and extremely so in ether or chloroform; on fusion with potassium hydroxide, it yields palmitic and acetic acids. Its sodium salt crystallises from alcohol in prisms soluble in water; the calcium salt (with H_2O) dissolves

slightly in alcohol; the *barium* salt is insoluble in water or alcohol, as is also the *silver* salt, which blackens in the light. The *ethyl* ester melts at 15°, distils unchanged at a temperature above 360°, and is miscible with the ordinary organic solvents. The *amide*,



crystallises from alcohol in prisms, melts at 107–108°, and dissolves readily in chloroform and, to a slight extent, in acetone or benzene.

βγ-Dibromostearic acid, $\text{CH}_3 \cdot [\text{CH}_2]_{14} \cdot \text{CHBr} \cdot \text{CHBr} \cdot \text{CO}_2\text{H}$, prepared by the action of bromine on Δ^{β} -oleic acid, separates from light petroleum in white prisms, melts at 71–72°, and dissolves in the ordinary organic solvents.

T. H. P.

Transformation of Sorbic Acid into Amino-acids. EMIL FISCHER and FRITZ SCHLOTTERBECK (*Ber.*, 1904, 37, 2357–2362).—E. Fischer and Roeder have shown (*Abstr.*, 1902, i, 124) that the amino-grouping in the aminobutyric acid, formed from crotonic acid by the action of ammonia, is in the β -position, whilst it has been shown by Wender that β -aminopropionic ethers result from the action of ammonia on esters of acrylic acid. The yield of amino-acid is, however, in such cases slight.

Whilst monoamino-acids can be synthesised by methods more convenient than that of the addition of ammonia to unsaturated acids, diamino-acids, especially those in which the amino-groups are in the 1:3- or 1:4-positions relatively to one another, are synthesised with more difficulty. The authors have accordingly studied the action of ammonia on sorbic acid, a type of unsaturated acid containing two double linkings, with the view of devising a general method for the syntheses of diamino-acids.

When sorbic acid is heated with an aqueous solution of ammonia at 130°, practically no addition of ammonia takes place; when, however, it is heated with a large excess of an aqueous solution of ammonia, saturated at 0°, for 20 hours at 150°, the main product is a yellow gum, which has a strongly alkaline reaction and is very easily soluble in water and in alcohol. It could not be obtained crystalline, but it shows all the characteristics of a diamino-acid and forms a crystalline *picrate*, $\text{C}_6\text{H}_{14}\text{O}_2\text{N}_2 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$, which melts at 185.5–186.5° (*corr.*). The acid in question is regarded as a diaminohectic acid, but is different from the known $\alpha\delta$ -diaminohectic acid (*i*-lysine). When it is heated for several hours at 150°, ammonia and water are evolved, and a substance is obtained which separates from ether in colourless prisms and melts at 109° (*corr.*), and is probably *aminohectic anhydride*, $\text{C}_6\text{H}_9\text{ON}$, derived from the unsaturated aminohectic acid, $\text{C}_6\text{H}_{11}\text{O}_2\text{N}$. The anhydride is easily soluble in water, alcohol, ethyl acetate, benzene, and pyridine, and is fairly stable towards bases; it is not changed when boiled for a short time with aqueous barium hydroxide, but, when heated for several hours with an excess of the latter, it is converted into an amino-acid, which has properties like those of pyrrolidinecarboxylic acid, and is possibly methylpyrrolidinecarboxylic acid.

In the synthetical diaminohectic acid, obtained in the manner

described, the amino-grouping is considered to be in the γ - or δ -position relatively to the carboxyl grouping.

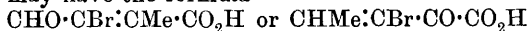
When β -vinylacrylic acid is heated with ammonia at 150° , it also forms a diamino-acid. A. McK.

Transformations of Salts of Pyruvic Acid. III. ANNE W. K. DE JONG (*Rec. trav. chim.*, 1904, 23, 131—146. Compare Abstr., 1901, i, 130; and 1902, i, 72).—The author has already shown that ammonium pyruvate is converted by pyruvic acid into α -acetylaminopropionic acid, and he now explains this transformation by assuming that the acid first formed, $\text{NH}:[\text{CMe}(\text{OH})\cdot\text{CO}_2\text{H}]_2$, becomes converted into the lactone, which loses first a molecule of carbon dioxide and then a molecule of water, forming α -acetylaminopropionic acid.

When a solution of pyruvic acid in water is neutralised with ammonium carbonate, the liquid after four days gives with phenylhydrazine a mixture of the phenylhydrazones of pyruvic and α -keto- γ -aminobutane- $\alpha\gamma$ -dicarboxylic acids. Eventually it becomes brown and deposits crystals of the ammonium salt of 2-methylpyridine-4:6-dicarboxylic acid. The latter, when prepared from the recrystallised sodium salt, is white and melts at 274° (compare Altar, Abstr., 1887, 378). When solutions of molecular quantities of pyruvic acid and ammonia in dilute alcohol are mixed, the resulting liquid becomes warm and deposits a white precipitate. A similar product is also formed when ammonia is used in excess. These precipitates give with phenylhydrazine a mixture of the phenylhydrazones of pyruvic and α -keto- γ -aminobutane- $\alpha\gamma$ -dicarboxylic acids, and the proportion of the phenylhydrazone of pyruvic acid formed is augmented if the precipitates are first boiled either with water or with dilute solution of ammonia. A tabular statement of the proportions of the two acids in these precipitates prepared under various conditions is given in the original. These products contain no metapyruvic or parapyruvic acids.

α -Keto- γ -aminobutane- $\alpha\gamma$ -dicarboxylic acid phenylhydrazone may be separated from the phenylhydrazone of pyruvic acid by washing with water and alcohol and recrystallising from boiling water. It forms spheroids of needles and melts and decomposes at 156° , is readily soluble in acids and alkalis, but only slightly so in ether, alcohol, and cold water. When the phenylhydrazone is warmed with hydrochloric acid of sp. gr. 1.14, it is converted into 3-keto-2-phenyl-4-methyl-2:3-dihydro-1:2-diazine-6-carboxylic acid (Abstr., 1902, i, 122). T. A. H.

Action of Hydrochloric Acid on Pyruvic Acid. IV. ANNE W. K. DE JONG (*Rec. trav. chim.*, 1904, 23, 147—154. Compare Abstr., 1901, i, 446; 1902, i, 122; 1903, i, 146).—When β -bromo- α -keto- Δ^{β} -butene- $\alpha\gamma$ -dicarboxylic acid is boiled under a reflux condenser with hydrochloric or sulphuric acid, carbon dioxide is evolved and an acid which may have the formula



is formed; this melts at 95° and is readily soluble in alcohol, ether, and chloroform. When β -bromo- α -keto- Δ^{β} -butene- $\alpha\gamma$ -dicarboxylic acid

is dissolved in acetic anhydride and the solution is evaporated under reduced pressure over sulphuric acid, a *mixed anhydride* of acetic acid and the α -lactone of β -bromo- α -keto- γ -hydroxybutane- α -dicarboxylic acid, $\text{CO} \begin{smallmatrix} \text{CHBr} \\ \diagup \quad \diagdown \\ \text{CO-O} \end{smallmatrix} \text{CMe} \cdot \text{CO} \cdot \text{OAc}$, is formed; this is crystalline and melts at 86° . A similar *product*, $\text{OAc} \cdot \text{CO} \cdot \text{CMe} : \text{CBr} \cdot \text{CO} \cdot \text{CO}_2\text{Et}$, is formed by the action of acetic anhydride on the monoethyl ester; this is an oil readily resolved by water into its generators. The formation of these anhydrides indicates that in the production of β -bromo- α -keto- Δ^2 -butene- α -dicarboxylic acid by the action of bromine on the α -lactone of α -keto- γ -hydroxybutane- α -dicarboxylic acid, the lactone ring is not broken by the introduction of the bromine atom, but by the action of the hydrogen bromide simultaneously formed.

Ethyl α -keto- Δ^2 -butene- α -dicarboxylate, $\text{CO}_2\text{Et} \cdot \text{CMe} : \text{CH} \cdot \text{CO} \cdot \text{CO}_2\text{Et}$, prepared by the action of hydrogen chloride on a solution of the lactone in alcohol, boils at 182 – 184° under 28 mm. pressure (compare Genvresse, Abstr., 1893, i, 552) and furnishes an oily *phenylhydrazone*.

The substance, $\text{C}_{12}\text{H}_{10}\text{O}_5\text{N}_2$, obtained by the action of hydrochloric acid on the phenylhydrazone of the α -lactone of α -keto- γ -hydroxybutane- α -dicarboxylic acid (Abstr., 1902, i, 122) gives with acetic anhydride an *acetyl* derivative which crystallises in colourless needles, melts and decomposes at 264° , and dissolves both in alcohol and in aqueous solution of sodium hydroxide with a yellow colour. From the substance, $\text{C}_{12}\text{H}_9\text{O}_4\text{N}_2 \cdot \text{H}_2\text{O}$, prepared from the foregoing compound by the action of sodium hydroxide, a *nitro*-derivative melting at 218° has been obtained.

T. A. H.

Preparation of Substituted Acylacetic Esters. LOUIS BOUEVAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1904, [iii], 31, 588–593. Compare Abstr., 1901, i, 311; 1902, i, 704; and 1903, i, 63 and 142).—Further details are given regarding the preparation of substituted acylacetic esters by the simultaneous action of alkyl haloids and sodium alkyloxides on the *C*-esters of the acylacetoacetates already described by the author (Abstr., 1902, i, 704). With primary alkyl iodides, a yield of 70–75 per cent. is obtained, and with the secondary iodides only 25–35 per cent., due to the formation of hydrogen iodide from these, which liberates the ester from its alkaline solution, and this is then hydrolysed forming either acetoacetic ester or an unsubstituted acylacetic ester. The alkyl bromides give smaller yields than the iodides.

The sodium alkyloxide (1 mol.) is dissolved in the ester, and after twelve hours the alkyl iodide is added and the mixture heated in closed vessels at 100 – 110° for at least six hours; the alcohol is distilled off and the residue washed with sodium carbonate and thio-sulphate and extracted with ether. The oil left on distilling off the ether is fractionated, the last fraction containing the required product.

The substituted acyl esters are colourless, mobile liquids; they give violet colorations with ferric salts, are insoluble in aqueous alkaline solutions, and show all the properties of β -ketonic esters. When dissolved in alcohol and heated for one hour at 100° with a slight

excess of hydrazine hydrate, they furnish disubstituted pyrazolones. The latter formed from complex esters are liquid, but distil with slight decomposition under reduced pressure; the others crystallise readily from boiling benzene or dilute alcohol and decompose slowly unless kept in closed vessels.

T. A. H.

Homologues of Butyrylacetic and *iso*Valerylacetic Esters.
RENÉ LOCQUIN (*Bull. Soc. chim.*, 1904, [iii], 31, 593—595. Compare Abstr., 1902, i, 704; 1903, i, 143 and preceding abstract).—The following esters were prepared by the general method described in the preceding abstract. Ethyl ethylbutyrylacetate, $\text{CPr}^{\alpha}\text{O}\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}$, obtained together with some ethyl ethylacetoacetate by the action of ethyl iodide and sodium ethoxide on ethyl *C*-butyrylacetate, boils at 105—108° under 13 mm. pressure and has a sp. gr. 0.975 at 0°/4° (compare Hamonet, Abstr., 1890, 235). When treated with hydrazine hydrate (compare Abstr., 1902, i, 704), it furnishes 4-ethyl-3-propylpyrazolone, which forms brilliant spangles, melts at 165—166° (corr.), and is soluble in ether, slightly so in water and benzene. From the small quantity of ethyl ethylacetoacetate present in the ester employed there was also formed in this reaction some 3-methyl-4-ethylpyrazolone, which crystallises in brilliant spangles and melts at 195—196° (corr.). Ethyl propylbutyrylacetate, $\text{CPr}^{\alpha}\text{O}\cdot\text{CHPr}^{\alpha}\cdot\text{CO}_2\text{Et}$, boils at 112—113° under 10 mm. pressure and has a sp. gr. 0.958 at 0°/4°. With hydrazine hydrate, it furnishes 3:4-dipropyl-5-pyrazolone which distils at 190—200° under 14 mm. pressure and gradually solidifies.

Ethyl isopropylbutyrylacetate, $\text{CPr}^{\alpha}\text{O}\cdot\text{CHPr}^{\beta}\cdot\text{CO}_2\text{Et}$, is produced only in small quantities by the general reaction; it boils at 111° under 14 mm. pressure, has sp. gr. 0.962 at 0°/4°, and with hydrazine hydrate furnishes 3-propyl-4-isopropyl-5-pyrazolone, which, in the slightly impure form in which it was obtained, melts at 133° (corr.).

Ethyl ethylisovalerylacetate, $\text{C}_4\text{H}_9\cdot\text{CO}\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}$, obtained from ethyl iodide and ethyl *C*-isovalerylacetoacetate (boiling point 122° under 12 mm. pressure. Compare Bouveault and Bongert, Abstr., 1903, i, 63), boils at 107—108° under 11 mm. pressure, has a sp. gr. 0.959 at 0°/4°, and furnishes with hydrazine hydrate 3-isobutyl-4-ethyl-5-pyrazolone, which forms slender needles, melts at 106° (corr.), and is soluble in ether.

T. A. H.

Homologues of Hexoylacetic and *iso*Hexoylacetic Esters.
RENÉ LOCQUIN (*Bull. Soc. chim.*, 1904, [iii], 31, 595—599. Compare Abstr., 1902, i, 704 and two preceding abstracts).—Ethyl methylhexoylacetate, $\text{C}_5\text{H}_{11}\cdot\text{CO}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$, obtained by the general method from ethyl *C*-hexoylacetate (*loc. cit.*), boils at 128—129° under 12 mm. pressure, has a sp. gr. 0.963 at 0°/4°, and with hydrazine hydrate furnishes 4-methyl-3-amylpyrazolone, which crystallises from boiling benzene in brilliant lamellæ and melts at 164—165° (corr.).

Ethyl sec-octylhexoylacetate, of which a yield of 27—30 per cent. was obtained, boils at 183—184° under 11 mm. pressure and has a sp. gr. 0.925 at 0°/4°. There are produced with this ester octylene, octyl alcohol, methyl amyl ketone, ethyl hexoate, ethyl octylacetoacetate, and ethyl hexoylacetic. The last-mentioned ester boils at 116—117°

under 20 mm. pressure and with hydrazine hydrate furnishes 3-amylpyrazolone (compare Bouveault and Bongert, Abstr., 1903, i, 143). On hydrolysis, it gives the corresponding solid acid, which crystallises from warm light petroleum in spangles and melts at 73–74°, decomposing at the same time into carbon dioxide and methyl amyl ketone.

Ethyl C-isohexoylacetoacetate, $C_5H_{11} \cdot CO \cdot CHAc \cdot CO_2Et$, prepared by Bouveault and Bongert's process (Abstr., 1903, i, 63), using a chloride (designated natural isohexoyl chloride) obtained from ordinary amyl alcohol, boils at 133–134° under 13 mm. pressure and has a sp. gr. 1.032 at 0°/4°. With methyl iodide it furnishes the corresponding *ethyl methylisohexoylacacetate*, which boils at 117–118° under 13 mm. pressure, has a sp. gr. 0.961 at 0°/4°, and furnishes a corresponding 4-methyl-3-isoamylpyrazolone; this crystallises in brilliant lamellæ from ether or benzene and in spangles from dilute alcohol and melts at 177–178° (corr.).
T. A. H.

Preparation of the Externally- and Internally-compensated Inactive Forms of 2:5-Dihydroxyadipic Acid. E. ROSENLEW (*Ber.*, 1904, 37, 2090–2092).—Two 2:5-dibromoadipic acids were prepared from adipic acid. One of these, designated as the *A* form, separates from formic acid in rosettes of compact leaflets and melts at 191°; it is insoluble in cold water and in boiling benzene, but is readily soluble in ether and in ethyl acetate; the *B* variety separates from formic acid in tiny crystals and melts at 138–139°; it is insoluble in benzene and light petroleum, but is readily soluble in water, ether, and ethyl acetate. By the action of baryta water, the hydroxy-acids corresponding with these dibromo-acids were prepared. *A*:2:5-Dihydroxyadipic acid separates from water in compact, transparent crystals and melts at 173°. *B*:2:5-Dihydroxyadipic acid separates from water in indistinctly crystalline forms and melts at 132–134°. Both acids are sparingly soluble in most organic solvents; the *A*-acid is more readily soluble in water than the *B*-acid. The *A*-acid is probably the externally-compensated, and the *B*-acid the internally-compensated form.
A. McK.

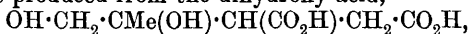
Transformation of Unsaturated Acids. RUDOLF FITTIG (*Annalen*, 1904, 331, 88–150. Compare Abstr., 1899, i, 332, 333, 417; and this vol., i, 418).—The oxidation of itaconic, aticonic, and mesaconic acids and their derivatives has been studied with the object of confirming the constitution assigned to these substances in previous communications (*loc. cit.*).

Oxidation of Dimethylitaconic and Dimethylaticonic Acids.—[With AUGUST SCHWÄRTZLIN.]—Dimethylitaconic acid (teraconic acid), $CM_e_2 \cdot C(CO_2H) \cdot CH_2 \cdot CO_2H$,

in the form of the sodium salt, was oxidised in dilute (1 per cent.) aqueous solution with 2 per cent. permanganate, the temperature not being allowed to rise above 2°. Acetone was isolated from the products of oxidation by fractionation of the alkaline liquid; acetic acid was the only volatile acid, and oxalic acid was found together with unchanged teraconic acid in the residue from the distillation.

Oxalacetic acid, which Fenton and Jones (Trans., 1900, 77, 77) had found to be very stable, was isolated from the products of oxidation, when the resulting alkaline liquor, the volume of which was kept small, was acidified, extracted with ether to remove unchanged teraconic acid, and then made strongly acid with sulphuric acid and again extracted with ether. It is thus shown that acetone and oxalacetic acid are the primary products of oxidation, and that the latter either breaks up, when heated in alkaline solution, into acetic acid and oxalic acid, or that it is partly further oxidised to malonic acid, which in its turn is oxidised to oxalic acid.

Dimethylitaconic acid, $\text{CH}_3 \cdot \text{CMe} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, was oxidised in the same manner as the last-mentioned acid; an odour of formaldehyde became at once perceptible, and the aldehyde was isolated by cautious distillation. Part of the liquid product of the oxidation was freed from acids by neutralisation with calcium carbonate, and then treated with ammonia and evaporated to dryness, the residue being extracted with ether, when hexamethylenetetramine was obtained, a fact which demonstrated the presence of formaldehyde in the original product. The remainder of the aqueous solution of the oxidation products was extracted first with ether and then with chloroform. From the latter solvent, *isoheptodilactone* (m. p. 116°) was obtained; it is doubtless produced from the dihydroxy-acid,



first formed, which is unstable in acid solution. The ethereal extract contained besides a small quantity of unchanged acid also small amounts of acetic acid, the only volatile acid, and lævulic acid (m. p. 32°), which was recognised by conversion into the silver and calcium salts. Formaldehyde and lævulic acid are the main products of the oxidation.

Oxidation of Hexylitaconic and Hexylitaconic Acids.—[With JOHANN SIMON.]—From the oxidation products of hexylitaconic acid, a small quantity of heptaldehyde was isolated by distillation in steam. The mother liquor was acidified with hydrochloric acid and extracted with ether several times. The first ethereal extracts contained unchanged hexylitaconic acid (m. p. 131°); the later extracts contained oxalic acid

and *hexylhydroxyparaconic acid*, $\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CH} \cdot \text{C}(\text{OH})(\text{CO}_2\text{H}) \cdot \text{CH}_2$,
 $\text{O} \text{---} \text{CO}$

which were separated by means of their calcium salts. The paraconic acid crystallises from ether in large plates belonging to the rhombic system [$a : b : c = 0.82241 : 1 : 1.48675$], and melting at $103\text{--}104^\circ$; the *barium* salt crystallises with H_2O , the *calcium* salt with $2\frac{1}{2}\text{H}_2\text{O}$, and the *silver* salt is anhydrous and amorphous.

When the salts of the paraconic acid are heated with excess of a solution of the alkali hydroxide, they are converted into the salts of *hexyltitartaric* acid; the *barium* salt, $\text{C}_{11}\text{H}_{18}\text{O}_6\text{Ba}$, is insoluble and amorphous, the *calcium* salt is similar. On setting free the acid from these salts, hexylitaconic acid was formed.

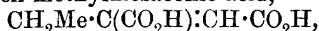
Hexylitaconic acid, which has been prepared from the hexylitaconic acid in a simpler manner than heretofore, was oxidised in the usual manner and yielded no aldehyde; the acidified liquor was extracted with ether; the unchanged hexylitaconic acid was removed as the

insoluble barium salt, and a new acid, $C_{11}H_{18}O_5$, isolated in the form of a soluble barium salt. This acid crystallises from ether and petroleum in needles melting at $126-127^\circ$, is dibasic, and, since it neither reacts with phenylhydrazine nor yields a lactone, appears to be the internal anhydride,

$$C_3H_5 \cdot \underset{O}{\overset{CH}{\parallel}} \rangle CH \cdot CH(CO_2H) \cdot CH_2 \cdot CO_2H, \text{ of a}$$

dihydroxy-acid; the *barium*, *calcium*, and *silver* salts are amorphous, anhydrous soluble powders. In the mother liquors from which the dibasic acid was separated, a *dilactone*, $C_{11}H_{18}O_4$, was found; it crystallises in needles melting and decomposing at $185-186^\circ$.

Oxidation of Methyl- and Ethyl-mesaconic Acids.—[With WILHELM DANNENBERG.]—When methylmesaconic acid,



is oxidised, methylpyruvic acid can readily be isolated by distilling in steam and converting the volatile acids into barium salts; its *phenylhydrazine* crystallises in pale yellow needles melting at $144-145^\circ$. Formic acid is also found in the distillate, and oxalic and malonic acids in the residue.

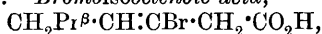
On oxidising ethylmesaconic acid and distilling the liquid in steam, formic and butyric acids can be isolated from the distillate in the form of calcium salts. The distillate also contains ethylpyruvic acid, which is purified by distilling the anhydrous mixture of acids obtained from the barium salts. The *barium* salt crystallises with H_2O in sparingly soluble, lustrous leaflets, the *calcium* salts with H_2O in small plates; the *silver* salt forms colourless needles; the *phenylhydrazine* crystallised in pale yellow needles melting and decomposing at $114-115^\circ$. The constitution of the ethylpyruvic acid was confirmed by reduction to α -hydroxyvaleric acid.

Action of Bromine on Methylitaconic and isoButylitaconic Acids.—[With OSCAR SHEEN.]—Methylitaconic acid is brominated by adding bromine to an aqueous suspension of the acid in ice-cold water; *methylitaconic acid dibromide*, $CHMeBr \cdot CBr(CO_2H) \cdot CH_2 \cdot CO_2H$, separates, whilst bromomethylparaconic acid remains in solution and can be isolated by extracting with ether, and crystallising the residue from the ether, from chloroform. The dibromide melts and decomposes at 178° , and, when warmed with water, is decomposed, yielding *methylaconic acid* and *bromo- Δ^{β} -pentenoic acid*, $CHMe \cdot CBr \cdot CH_2 \cdot CO_2H$, which is separated from the methylaconic acid by its greater solubility in a mixture of chloroform and petroleum; the latter acid crystallises in lustrous plates melting at 54° , and was proved to have the foregoing constitution by reducing it to Δ^{β} -pentenoic acid by means of sodium amalgam; further, the pentenoic acid on bromination yields $\beta\gamma$ -dibromovaleric acid (m. p. $65-65.5^\circ$).

Bromomethylparaconic acid, $O \langle \underset{CO-CH_2}{\overset{CHMe \cdot CH}{\parallel}} \rangle CBr \cdot CO_2H$, forms only a small part of the product of bromination of methylitaconic acid, and crystallises in cubes melting and decomposing at 138° ; on reduction, it is converted into methylparaconic acid. On boiling bromomethylparaconic acid with water, *methylaconic acid*, $O \langle \underset{CO-CH}{\overset{CHMe}{\parallel}} \rangle C \cdot CO_2H$, is formed; it crystallises in small prisms melting at $159.5-160^\circ$; its

barium salt forms anhydrous needles and the *calcium* salt is amorphous. On reduction with sodium amalgam, it is converted into methylparaconic acid.

[With JACOB KRAENCKER.]—*iso*Butylitaconic acid, when brominated in the same manner as the methylitaconic acid, yields mainly a dibromide, $C_4H_9 \cdot CHBr \cdot CBr(CO_2H) \cdot CH_2 \cdot CO_2H$, and *bromoisobutylparaconic acid*, $O \left\langle \begin{array}{c} CH(C_4H_9) \\ CO-CH_2 \end{array} \right\rangle CBr \cdot CO_2H$. These are separated by adding chloroform to the ethereal solution, when the dibromide separates first; it forms crystalline aggregates melting and decomposing at $168-171^\circ$; when boiled with water, it is decomposed yielding *bromo-isooctenoic acid*, *isobutylaconic acid* (m. p. 170°), which forms the main solid constituent of the mixture, and *isobutylparaconic acid*. *Bromoisobutylparaconic acid* crystallises in needles melting and decomposing at $144-145^\circ$. *Bromoisooctenoic acid*,



which forms the main product of the decomposition of the dibromo-acid with water, and is separated from the two solid products of the reaction, *isobutylaconic acid* and *isobutylparaconic acids*, by extraction with petroleum, is purified by distillation in steam, and forms white crystals melting at $14-15^\circ$. On reduction with sodium amalgam, it was converted into *isooctenoic acid* (b. p. $231-232^\circ$), which was then transformed into *isooctolactone*. K. J. P. O.

A Crystalline Chromous Tartrate. GEORGES BAUGÉ (*Compt. rend.*, 1904, 138, 1217—1220).—The author has obtained an anhydrous, blue, crystalline chromous tartrate, $CrC_4H_4O_6$, by the action of tartaric acid on moist chromous acetate (compare Moissan, *Abstr.*, 1881, 684, 685; 1883, 22). As the salt is readily oxidised, a special apparatus, not yet described, was used, whereby the whole operation, including the filtering and washing, was performed in an atmosphere of carbon dioxide. The salt has a sp. gr. of 2.33 at 15° , is insoluble in cold or boiling water, or water saturated with carbon dioxide, is not acted on by dry chlorine in the cold, but decomposed into chromium sesquioxide and carbon at a slightly higher temperature; is attacked by hydrogen sulphide at a red heat with the formation of a black sulphide and liberation of hydrogen, and is decomposed with the formation of the sesquioxide by the action of dry hydrogen, hydrogen chloride, sulphur dioxide, ammonia, or carbon dioxide at a red heat. Chromous tartrate readily reduces an ammoniacal solution of silver nitrate in the cold, whilst the neutral nitrate is decomposed but slowly. Concentrated solutions of alkali carbonates decompose the tartrate in the cold, forming double carbonates of chromous oxide; if, however, dilute solutions of the carbonates are employed in large excess, the chromous salt is converted quantitatively into chromic oxide (compare *Abstr.*, 1900, ii, 349). M. A. W.

Preparation of $\alpha\beta$ -Diketonic Esters. LOUIS BOUEVAULT and ANDRÉ WAHL (*Compt. rend.*, 1904, 138, 1221—1223).—The method of preparing a ketonic ester by the action of nitrogen peroxide on the corresponding *isonitroso*-compound, as used in the case of the *iso*-

nitrosomalonic esters (compare Abstr., 1903, i, 677), appears to be of general application. *Ethyl diketobutyrate*, $\text{COMe} \cdot \text{CO} \cdot \text{CO}_2\text{Et}$, prepared by the action of nitrous gases on a solution of ethyl isonitrosoacetoacetate in acetic anhydride, is a mobile, orange-yellow liquid boiling at 70° under 13 mm. pressure, possessing the ethereal odour characteristic of diketones, and reacting energetically with water to form a colourless crystalline *hydrate*, $\text{COMe} \cdot \text{CO} \cdot \text{CO}_2\text{Et} \cdot \frac{1}{2}\text{H}_2\text{O}$, which crystallises from anhydrous ether in beautiful, white needles melting at 120° , and is probably identical with the compound obtained by Sachs and Wolff (compare Abstr., 1903, i, 793) by saponifying the condensation product of nitrosodimethylaniline and ethyl acetoacetate. *Ethyl diketobutyrate phenylhydrazone* crystallises in clear yellow prisms melting at $102\text{--}103^\circ$.

isoButyl diketobutyrate, prepared similarly to the ethyl compound, is an orange-yellow liquid boiling at $96\text{--}100^\circ$ under 18 mm. pressure; it forms a colourless, crystalline *hydrate*, $\text{C}_8\text{H}_{12}\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, melting at 96° , a *disemicarbazone* in the form of a white, crystalline powder melting at $254\text{--}255^\circ$ and almost insoluble in the ordinary solvents, and a *phenylhydrazone* crystallising in yellow, rhombohedral plates, melting at $98\text{--}99^\circ$.
M. A. W.

New Polymerides of Formaldehyde. ALPHONSE SEYEWETZ and GIBELLO (*Compt. rend.*, 1904, 138, 1225—1227).—By the action of heat on a mixture of trioxymethylene and water, the author has obtained four polymerides of formaldehyde, which differ in solubilities and melting points from paraformaldehyde, its hydrate, α -trioxymethylene, or ordinary trioxymethylene. The new polymerides are separated by fractional distillation: the first forms a crystalline sublimate in the reflux apparatus, melts at 123° , is soluble in cold water, slightly soluble in boiling alcohol, almost insoluble in ether, and five times as soluble as ordinary trioxymethylene in sodium sulphite solution; the second separates in white flakes from the aqueous distillate, melts at $96\text{--}97^\circ$, is soluble in cold water, slightly soluble in boiling alcohol, insoluble in ether, and equally soluble as the preceding compound in sodium sulphite solution; the third is extracted by ether from the aqueous mother liquors from which the second is deposited; it melts at 69° , is soluble in water, fairly so in alcohol, and with the exception of α -trioxymethylene (m. p. $60\text{--}61^\circ$) is the only polymeride of formaldehyde that is soluble in ether; the fourth polymeride separates as white crystals from the liquid left in the flask after the distillation, melts at $92\text{--}93^\circ$, is soluble in cold water or boiling alcohol, and insoluble in ether; on being heated, it partly sublimes unchanged, and is partly converted into the trioxymethylene melting at $170\text{--}171^\circ$. Attempts to discover the molecular complexity of these new compounds by molecular weight determinations were unsuccessful; the vapour density method gave in all cases numbers approximating to 30, whilst the cryoscopic method with freshly prepared solutions gave the number 60.
M. A. W.

Action of Phosphorus Pentachloride on Chloral. F. GIOLITTI (*Gazzetta*, 1904, 34, i, 247—253).—The action of phosphorus penta-

chloride on chloral yields (1) a compound, $\text{CCl}_3 \cdot \text{CH} \begin{smallmatrix} \diagup \text{O} \diagdown \end{smallmatrix} \text{PCl}_3$, which is an oily liquid having a pungent odour, fuming in the air, and boiling at $238-242^\circ$; it has the normal molecular weight in freezing benzene and the normal vapour density under diminished pressure; salts of silver precipitate half the chlorine it contains; (2) a small quantity of tetrachloroethylene.

T. H. P.

The Alkyl Allyl and Propenyl Ketones. EDMOND E. BLAISE (*Compt. rend.*, 1904, 138, 1106—1108. Compare this vol., i, 290, 370).—Owing to the greater readiness with which the ethylenic linking in the $\alpha\beta$ -position becomes saturated than the same linking in the $\beta\gamma$ -position, the alkyl allyl ketones ($\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{COR}$) and the isomeric alkyl propenyl ketones ($\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{COR}$) behave differently towards such reagents as hydroxylamine and semicarbazide; the alkyl allyl ketones yield the normal oxime and semicarbazone respectively, whilst the alkyl propenyl ketones give with hydroxylamine oximes isomeric with the alkyl allyl oximes, and also soluble hydroxylaminoximes yielding dibenzoyl derivatives, and with semicarbazide semicarbazido-semicarbazones (compare Power and Lees, *Trans.*, 1904, 85, 635).

The dibromo-derivatives formed by the action of bromine on the two types of unsaturated ketones are unstable liquids that cannot be distilled; on treatment with a solution of an alkali carbonate, the brominated alkyl allyl ketones yield a colourless distillate, whilst brominated alkyl propenyl ketone gives an α -diketone which is readily characterised by its intense greenish-yellow colour and the formation of an osazone.

M. A. W.

Starch Conversion in the Mash Tun. ARTHUR R. LING (*J. Fed. Inst. Brewing*, 1903, 9, 446—461).—As the compounds known as malto-dextrins are simply carbohydrates of less complexity than those to which the name dextrin has been applied, the author suggests that the term malto-dextrin be adopted for the whole class of diastatic products, since it indicates their origin and avoids confusion with the dextrin of torrefaction.

Brown, Morris, and Millar have stated that the malto-dextrin obtained by them, which is identical with the malto-dextrin α of Ling and Baker (*Trans.*, 1897, 71, 514), is completely converted into maltose by the action of diastase, but the author finds that this compound (having the constants $[\alpha]_{\text{D}_{53-93}} 180.5^\circ$ and $R_{\text{D}_{53-93}} 36.7$) yields a mixture containing approximately 90 per cent. of maltose and 10 of dextrose when subjected to the action of active diastase prepared from a low-dried malt for 140 hours at 131°F . The maximum proportion of dextrose appears never to exceed 12 per cent. of the total products, and when this maximum has been reached, further heating at 131° with the enzyme produces a diminution in the amount of this sugar.

Dextrose is formed when starch paste is treated for a long time with diastase solution, but only when the latter has been previously heated to above 140°F . When, however, the products of the partial hydrolysis of starch by diastase unrestricted by heat are isolated and

submitted to the further action of the enzyme, dextrose is always obtained.

The diminution in the amount of dextrose occurring on prolonged action of diastase is attributed to the synthetic action of the enzyme. Dextrose itself, however, could not be made to undergo this condensation change. Lintner's isomaltose may possibly be a reversion product of dextrose.

Mashes made with malt starch and with barley starch of various origins, at temperatures below that at which the starch employed gelatinises, show that the changes taking place are considerably different from starch paste conversions, and the results make it probable that the starch undergoes hydrolysis without preliminary gelatinisation.

T. H. P.

Analogy between Organic Oxygen and Nitrogen Compounds. W. TSCHELINZEFF (*Ber.*, 1904, 37, 2081—2085).—The author compares different groups of oxygen and nitrogen derivatives as regards their reactions with organo-magnesium compounds, for example, water with ammonia, alcohols with amines (primary and secondary), carbon dioxide with carbylamines, ketones with nitriles, acids with amides, and esters of formic acid with alkylated formamides.

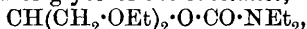
The analogy extends even further, for dimethylaniline can take the place of ether as a solvent in the preparation of Grignard's compounds.

J. J. S.

Electrolysis of Tetraethylammonium Iodide. EMIL GOECKE (*Zeit. Elektrochem.*, 1904, 10, 249).—When a solution of tetraethylammonium iodide is electrolysed with platinum electrodes, the main product is tetraethylammonium tri-iodide, NEt_4I_3 . Small quantities of iodoform are also produced.

T. E.

Action of Chloro-formdiethylamide on Alcohols and Phenols. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and F. PERRIN (*Bull. Soc. chim.*, 1904, [iii], 31, 689—691).—Chloro-formdiethylamide, prepared by Michler and Escherich's method (*Abstr.*, 1879, 934), reacts with alcohols and phenols to produce a series of compounds of the type $\text{RO}\cdot\text{CO}\cdot\text{NEt}_2$. With ethyl alcohol, *ethyl diethylcarbamate*, $\text{EtO}\cdot\text{CO}\cdot\text{NEt}_2$, a liquid boiling at $169\text{--}172^\circ$, is formed; with diethylcarbinol, the *product*, $\text{C}_6\text{H}_{11}\text{O}\cdot\text{CO}\cdot\text{NEt}_2$, a liquid boiling at $206\text{--}208^\circ$, is formed, and from symmetrical dichlorohydrin the *substance*, $\text{C}_3\text{H}_5\text{Cl}_2\text{O}\cdot\text{CO}\cdot\text{NEt}_2$, which boils at $259\text{--}261^\circ$ and is insoluble in water, is obtained; and with the diethyl ether of glycerol the *substance*,



is produced; it is insoluble in water and boils at $260\text{--}262^\circ$.

Phenyl diethylcarbamate, $\text{PhO}\cdot\text{CO}\cdot\text{NEt}_2$, similarly prepared from phenol, is a viscous liquid which boils at $270\text{--}271^\circ$ and is insoluble in water. From resorcinol, the *substance*, $\text{C}_6\text{H}_4(\text{O}\cdot\text{CO}\cdot\text{NEt}_2)_2$, a viscous liquid, insoluble in water and boiling at $263\text{--}267^\circ$, is obtained, and with guaiacol the *product*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{NEt}_2$, which boils at $299\text{--}300^\circ$ and otherwise resembles the foregoing compounds, is procured.

T. A. H.

A Naturally-occurring Isomeride of Leucine. I. FELIX EHRLICH (*Ber.*, 1904, 37, 1809—1840. Compare Abstr., 1903, i, 796).—The preparation of *d*-isoleucine from beet sugar is fully described. From the liquors to which the strontia desaccharification process has been applied, a mixture of *r*-leucine, *l*-leucine, and *d*-isoleucine was obtained, from which the latter may be isolated by aid of its copper derivative, which differs from the copper salt of leucine in its great solubility in methyl alcohol.

d-isoLeucine hydrochloride forms stellate needles. The copper salt of *d*-isoleucine separates in leaflets, grouped in rosettes; it is very readily soluble in benzyl alcohol, ethyl acetoacetate, or benzaldehyde. When heated at 180° with baryta solution, *d*-isoleucine is completely racemised. The copper salt of *r*-isoleucine is also readily soluble in methyl alcohol. The benzoyl, benzenesulphonic, phenylcarbimide, and hydantoin compounds of *d*-isoleucine were prepared by the methods used by E. Fischer for the corresponding derivatives of *l*-, *d*-, and *r*-leucines respectively, and are well adapted for the characterisation of *d*-isoleucine. The phenylhydantoin derivative, prepared by the action of hydrochloric acid on the phenylcarbimide, separates from light petroleum in silky needles and melts at 78—79°. As distinct from other derivatives of *d*-isoleucine, it is laevorotatory.

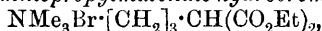
d-isoLeucine was also isolated from the products of the action of pancreatic juice on blood fibrin. It has also been isolated as a product resulting from the hydrolysis of ovalbumin by sulphuric acid, from the crude leucine obtained by the putrefaction of beef, and from other sources. The conclusion is drawn that *d*-isoleucine almost invariably occurs along with *l*-leucine as a primary product of proteid hydrolysis.

d-isoLeucine is not identical with *d*-α-amino-*n*-hexoic acid.

The reason why previous investigators have found the isolation of *l*-leucine so difficult is that *d*-isoleucine is also present, and the two isomerides form mixed crystals. About equal parts of *d*-isoleucine and partially racemised *l*-leucine are present in the liquors, to which the strontia desaccharification process has been applied. A. McK.

Betaines. III. δ-Trimethylvalerobetaine. RICHARD WILL-STÄTTER and WALTER KAHN (*Ber.*, 1904, 37, 1853—1858. Compare Abstr., 1902, i, 266; this vol., i, 235).—Although, when heated, α-betaines undergo rearrangement into isomeric esters of tertiary amino-acids, β- and γ-betaines split off trimethylamine. The simplest type of δ-betaine, that derived from trimethylaminovaleic acid, has now been studied.

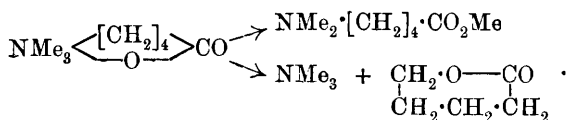
Ethyl δ-trimethylaminopropylmalonate hydrobromide,



prepared from ethyl δ-bromopropylmalonate and trimethylamine, forms white, hygroscopic crystals, and, when boiled with alkali, does not yield the amine. When heated with an excess of fuming hydrobromic acid for four hours at 130°, it forms δ-trimethylaminovaleic hydrobromide, $\text{NMe}_3\text{Br}\cdot[\text{CH}_2]_4\cdot\text{CO}_2\text{H}$, which separates from ethyl alcohol in transparent, flat plates and melts at 184—187°. δ-Trimethylvalerobetaine, $\text{NMe}_3\cdot\left[\text{CH}_2\right]_4\text{CO}$, prepared by treating δ-trimethylamino-

valeric hydrobromide with freshly precipitated silver oxide, separates from ethyl alcohol in brilliant, hexagonal plates, which contain $2\text{H}_2\text{O}$ and melt at $126\text{--}127^\circ$. When dehydrated, it softens at over 200° and melts and decomposes at about 228° . Its *picrate* melts at $158\text{--}159^\circ$; its *platinichloride* melts and decomposes at 225° .

When δ -trimethylvalerobetaine is heated at $230\text{--}240^\circ$, trimethylamine is evolved and the liquid distillate consists mainly of the isomeric methyl dimethylaminovalerate, and in this respect the δ -resembles the α -betaine. The analogy, however, with γ -betaine is indicated by the presence in the distillate of small amounts of δ -valerolactone. The comportment of the δ -betaine, when heated, may accordingly be represented as follows :



The δ -valerolactone obtained was identified by its boiling point, 215° (uncorr.).

Methyl δ -dimethylamino-n-valerate, $\text{NMe}_3 \cdot \text{[CH}_2\text{]}_4 \cdot \text{CO}_2\text{Me}$, boils at $186\text{--}189^\circ$ and has a strongly alkaline reaction; it is readily hydrolysed by contact with cold water for several days. Its *aurichloride* melts at 75° .
A. McK.

Betaines. IV. Behaviour of Aromatic Betaines towards Sodium Amalgam. RICHARD WILLSTÄTTER and WALTER KAHN (*Ber.*, 1904, 37, 1858—1860. Compare preceding abstract).—Aliphatic betaines, with the single exception of β -propiobetaine, are not acted on by sodium amalgam, even when their solutions are boiled with it; on the other hand, certain aromatic betaines are converted by sodium amalgam into the amine and acid, thus the three benzobetaines, even in the cold, are quantitatively reduced to benzoic acid and trimethylamine. Sodium amalgam has no action on phenyldimethylglycine. The reduction product from the experiments with *o*- and *p*-benzobetaines was contaminated with unsaturated hydrobenzoic acids. The amine was identified in each case by its aurichloride and platinichloride.

Aromatic amino-acids with primary, secondary, or tertiary basic groups are not attacked by sodium amalgam, with the exception of dimethylantranilic acid, from which dimethylamine may be obtained in small amount.
A. McK.

Optically Isomeric Malonobenzylamic Acids. OSCAR LUTZ (*Ber.*, 1904, 37, 2123—2129. Compare Abstr., 1902, 596 and 698).—*l*-Bromosuccinic acid dissolved in methyl alcohol condenses with benzylamine to *benzylamine d*- β -malonobenzylamate, which melts at $152\text{--}153^\circ$, and has $[\alpha]_D + 31.4^\circ$ in methyl alcohol and $+28^\circ$ in water. *d*- β -Malonobenzylamic acid crystallises in glistening plates, melts and decomposes at $130\text{--}131^\circ$, has a sp. gr. 1.347 at $18^\circ/4^\circ$, and $[\alpha]_D + 13.6^\circ$ in methyl alcohol. The sodium salt has $[\alpha]_D + 33.8^\circ$ in water, and the monobenzoyl derivative melts at 125° . *l*- β -Malonobenzylamic acid,

prepared in a similar manner from *d*-chlorosuccinic acid melts at 130—131°, has a sp. gr. 1.349 at 18°/4°, and $[\alpha]_D -13.8^\circ$ in methyl alcohol. *i*- β -malonobenzylamic acid, prepared from *i*-bromosuccinic acid, melts at 159—160°, has a sp. gr. 1.360 at 18°/4°, forms a benzoate melting at 116°, and an acetate melting at 111°. Silver *l*-malonobenzylamate reacts with methyl iodide to form methyl *l*-malonobenzylamate, which crystallises in plates melting at 105°, has $[\alpha]_D -12.8^\circ$ in methyl alcohol, and unites with benzylamine in cold alcoholic solution to form *l*-malic acid dibenzylamide; this crystallises in plates, melts at 157°, and the saturated methyl-alcoholic solution has $[\alpha]_D -36.9^\circ$.

E. F. A.

Preparation of Calcium Cyanamide. CYANID-GESELLSCHAFT IN BERLIN (D.R.-P. 150878).—Calcium cyanamide is best prepared by passing nitrogen over a heated mixture of lime or other calcium compounds with carbon, an excess of carbon or carbonaceous matter being advantageous. The temperature at which the formation of cyanamide occurs is much higher than when previously prepared calcium carbide is employed (2000° instead of 800—1000°), but is below that needed for the production of carbide.

C. H. D.

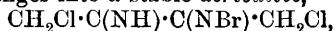
Preparation of Cyanides from Ferrocyanides. GROSSMANN'S CYANIDE PATENTS SYNDICATE (D.R.-P. 150551).—In the preparation of hydrocyanic acid from potassium ferrocyanide and dilute sulphuric acid, one-half of the cyanogen remains behind in the form of ferrous potassium ferrocyanide ("Everitt's salt"), and can only be very imperfectly reconverted into ferrocyanide by the action of alkali hydroxide. If, however, a slight excess of alkali hydroxide is added, and air is blown through the suspended mass, the conversion into ferrocyanide takes place rapidly and quantitatively. The remaining iron is precipitated in the form chiefly of triferrous tetroxide.

C. H. D.

Chlorinated Acetonitriles. JULIUS TROEGER and OTTO LÜNING (*J. pr. Chem.*, 1904, [ii], 69, 347—358. Compare Troeger, *Abstr.*, 1895, i, 161).—Reduction of triperchloromethyltriazine (Tscherven-Iwanoff, *Abstr.*, 1891, 1332) by zinc dust in alcoholic solution leads to the formation of ammonia, acetic acid, and an alkaline oil which forms a crystalline *platinichloride* containing 41.98 per cent. of platinum.

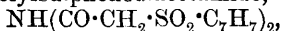
When hydrogen chloride is passed through chloroacetonitrile in ethereal solution, a crystalline additive compound is formed (Weddige and Körner, *Abstr.*, 1885, 739). This substance decomposes to chloroacetonitrile and hydrogen chloride on exposure to air. If the ether is omitted and the product preserved in a sealed tube, *chloroacetimide chloride*, $\text{CH}_2\text{Cl}\cdot\text{CCl}\cdot\text{NH}$, separates in crystals after some days. The action of water on chloroacetimide chloride leads to the formation of ammonium chloride and *s*-dichlorodiacetamide (König, this vol., i, 296), which melts at 195°.

Chloroacetonitrile and hydrogen bromide form an unstable additive compound, which decomposes on exposure to air or in a vacuum, but in a sealed tube changes into a stable derivative,



which forms white, microscopic crystals, melts at 143° , and, when acted on by water, yields *s*-dichlorodiacetamide.

With sodium *p*-tolylsulphinate in alcoholic solution, dichlorodiacetamide yields *p*-ditolylsulphonediacetamide,



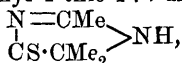
which melts at 164° .

G. Y.

α -Acetylaminoisobutyronitrile. GUSTAF HELLSING (*Ber.*, 1904, 37, 1921—1925).—Jay and Curtius' method for the preparation of α -aminonitriles by the action of ammonium cyanide on aldehydes (*Abstr.*, 1894, i, 162) may also be extended to ketones.

α -Acetylaminoisobutyronitrile, $\text{CN}\cdot\text{CMe}_2\cdot\text{NHAc}$, prepared by adding acetone to a solution of ammonium cyanide and adding acetic anhydride to the unstable, oily α -aminoisobutyronitrile at first produced, crystallises from ether in transparent, rectangular tablets or needles and melts at 106° . **Potassium α -acetylaminoisobutyrate**, $\text{C}_6\text{H}_{10}\text{O}_3\text{NK}$, obtained by hydrolysis of the nitrile, forms transparent prisms and melts and decomposes at 133° . Alcoholic hydrogen chloride converts the nitrile into *ethyl α -acetylaminoisobutyrate*, $\text{C}_8\text{H}_{15}\text{O}_3\text{N}$, crystallising in colourless prisms and melting at $87\cdot5^{\circ}$.

Alcoholic ammonium sulphide converts the nitrile into **α -acetylaminothioisobutyramide**, $\text{NHAc}\cdot\text{CMe}_2\cdot\text{CS}\cdot\text{NH}_2$, crystallising from water in colourless prisms, and melting and decomposing at 162° . When heated for some time above this temperature, water is evolved, and a compound, $\text{C}_6\text{H}_{10}\text{N}_2\text{S}$, is obtained crystallising in large, transparent leaflets, melting at 163° , and forming a yellow *hydrochloride*, which decomposes above 200° . The elimination of water may take place in one of two ways, the thioamide reacting in the amino-form, and yielding 2 : 5 : 5-trimethyl-4-thio-4 : 5-dihydroglyoxaline,



or in the imino-form, yielding a thiazole derivative. This point is under investigation.

C. H. D.

Ethyl isoCyanide Dibromide. H. GUILLEMARD (*Bull. Soc. chim.*, 1904, [iii], 31, 605—610. Compare Tchneriac, *Abstr.*, 1878, 132, and Nef, *Abstr.*, 1892, 1438).—When *ethyl isocyanide* (1 mol.), dissolved in chloroform, is treated with bromine (1 mol.) dissolved in the same solvent, ***ethyl isocyanide dibromide***, $\text{NEt}\cdot\text{C}\cdot\text{Br}_2$, is formed; this crystallises, when freed from any trace of solvent by exposure with suitable absorbents under reduced pressure, distils at 100° under 165 mm. pressure, at 93 — 94° under 110 mm. pressure, and at 145 — 147° under atmospheric pressure; if, however, the latter temperature be exceeded, decomposition ensues with the formation of a black, resinous residue and a white, crystalline sublimate.

Water converts the dibromide into ethylamine hydrobromide. With hydrogen sulphide, ***ethyl isocyanide dibromide hydrobromide*** and ***ethylthiocarbimide*** are formed. The latter is also obtained by the action of metallic sulphides. Dry hydrogen chloride passed through a solution of the dibromide in carbon disulphide, furnishes the *hydrochloride*, which, like the hydrobromide, is colourless and

crystalline. With ethyl iodide, an oily *ethiodide* is produced. The action of alcohol on the dibromide dissolved in carbon disulphide is similar to that of water, but there are also formed ethyl bromide and ethylcarbimide hydrobromide. With mercuric oxide, ethylcarbimide is produced. When dry ammonia is passed into a solution of the dibromide in chloroform, ammonium bromide is precipitated and a *base*, $C_6H_{12}N_4$ is formed, which crystallises in colourless needles, melts at $90-94^\circ$, is soluble in alcohol, insoluble in water and benzene, and furnishes crystalline *salts* and a slightly soluble *picrate* and *platini-chloride*. To this product, the author assigns the formula



Similar substances are produced with methylamine and aniline.

T. A. H.

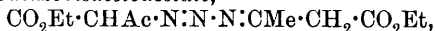
Diazo-fatty Acids. ANGELO ANGELI (*Ber.*, 1904, 37, 2080—2081).—A claim for priority (compare Abstr., 1893, i, 261, and Curtius and Müller, this vol., i, 481).

J. J. S.

Diazotisation of Hydrazine. II. MARIO BETTI (*Gazzetta*, 1904, 34, i, 201—212. Compare Abstr., 1903, i, 78).—*Bisdiazoacetone*, $N_4(CH_2Ac)_2$, obtained in place of ethyl bisdiazoacetate (*loc. cit.*), under certain conditions of diazotisation of hydrazine in presence of ethyl acetoacetate, crystallises from alcohol in golden-yellow, silky needles, melts and decomposes at 228° and is soluble in methyl or amyl alcohol or acetone and, with partial decomposition, in water. It sublimes, with slight decomposition, yielding white, silky crystals which have the melting point 228° , and forms yellow needles when crystallised from alcohol. It is soluble in moderately concentrated alkali hydroxide solution, from which it is precipitated unchanged by the addition of acid. The *sodium salt*, $C_6H_8O_2N_4Na_2$, yields a strongly alkaline aqueous solution which gives precipitates with various metallic salts. Its *dibenzoyl derivative*, $N_4(CHBzAc)_2$, crystallises from alcohol in long, golden needles melting at 170° . *Bisdiazoacetone* has the normal molecular weight in boiling ethyl acetate solution. When boiled with dilute hydrochloric acid, it yields nitrosoacetone, acetone, and a large proportion of methylglyoxime.

Under still other conditions of diazotisation, in presence of ethyl acetoacetate, hydrazine yields: (1) a small proportion of ethyl bisdiazoacetate and

(2) *Ethyl azodiazobisacetoacetate*,



which crystallises from aqueous alcohol in pale greenish-yellow, nacreous, rhombohedral plates melting and decomposing at 140° . It has an acid reaction and exhibits normal ebullioscopic behaviour in benzene. With hydrochloric acid, it yields, like ethyl bisdiazoacetate, *isonitrosomethylpyrazolone*.

T. H. P.

Basic Properties of Cacodylic Acid and of Carbamide. JAN VON ZAWIDZKI (*Ber.*, 1904, 37, 2289—2298. Compare this vol., i, 232; Hantzsch, this vol., i, 381).—That cacodylic acid has no dibasic tendency is shown by a comparison with carbonic acid, a weak,

dibasic acid which has a dissociation constant ($K = 3.04 \times 10^{-7}$ for $\text{HCO}_3\cdot\text{H}$) similar to that of cacodylic acid ($K = 4.2 \times 10^{-7}$). On mixing solutions of potassium hydrogen carbonate and potassium hydroxide, the electrical conductivity is 56.4 per cent. less than that calculated by a simple additive rule, whereas in the case of sodium cacodylate the decrease is 10 per cent., with sodium chloride, 4 per cent., and with sodium acetate 5.5 per cent.

No conclusion as to the character of the basicity of cacodylic acid can be drawn from a comparison with dimethylpyrone, as the basic nature of the latter is equally unexplained. From its accelerating effect on the bi-rotation of lactose, the dissociation constant of cacodylic acid as a base is found to be 1.35×10^{-13} . This agrees well with the dissociation constants for cacodylic acid calculated from the hydrolysis of its hydrochloride, and from its effect on the bi-rotation of dextrose. It is shown that there is a similar agreement between the dissociation constants for carbamide obtained by these different methods.

Abnormal temperature coefficients for the dissociation constants of weak bases are not uncommon. For carbamide at 25° , $K = 1.5 \times 10^{-14}$; at 40.2° , $K = 3.7 \times 10^{-14}$ (Wood, Trans., 1903, 83, 568). G. Y.

Substitution in the Benzene Nucleus. JAN J. BLANKSMA (*Rev. trav. chim.*, 1904, 23, 202—217. Compare Armstrong, Trans., 1887, 51, 258, and 1900, 77, 104; Crum Brown and Gibson, *ibid.*, 1892, i, 61, 367; Chattaway and Orton, *ibid.*, 1901, 79, 274; Vorländer, Abstr., 1902, i, 328; Flürscheim, Abstr., 1903, i, 79; and Holleman, Abstr., 1903, i, 623).—The author has already given expression to the view, which is in harmony with the ideas enunciated by Hantzsch, Bamberger, and Chattaway and Orton, that direct substitution in the benzene nucleus gives rise to the formation (principally) of meta-compounds, and indirect substitution to a mixture of ortho- and para-derivatives (Abstr., 1902, i, 600. Compare Lobry de Bruyn, this vol., i, 388). In extension of this, he now suggests that the following rule is generally applicable. When the nucleus contains two or three of any one of the groups NH_2 , OH , or Me or any possible combinations by twos or threes of these three groups in the positions 1, 3, and 5, it is possible to introduce under determinate conditions the groups Me , $\text{CH}_2\cdot\text{OH}$, CH_2Cl , CHO , CHCl_2 , CO_2H , CCl_3 , Ac , Bz , HSO_3 , I , Br , Cl , NO_2 or NO or N:NPh , &c., and so much the more easily as there are more of the groups Me , NH_2 , and OH present in the nucleus. Conversely, the elimination of certain groups is similarly favoured by the number of Me , NH_2 , or OH groups present in the nucleus.

A large number of illustrative instances of the applicability of this rule are given in the original. T. A. H.

Interaction occurring between Aluminium, Mercuric Chloride, and Benzene. WLADIMIR VON GULEWITSCH (*Ber.*, 1904, 37, 1560—1564).—When aluminium turnings are added in a reflux apparatus to benzene containing mercuric chloride, a very vigorous

action occurs; on slow evaporation of the filtered product, large, transparent, six-sided plates separate which have the composition $C_6H_5AlCl_3.HgCl$; the compound formed is hygroscopic, and is decomposed by water giving benzene, mercurous chloride, and some mercury.

In the formation of the compound, mercurous chloride is initially produced according to the equation: $3Al + 6HgCl_2 = 3AlCl_3.HgCl + 3Hg$; the amount of mercury liberated corresponds sufficiently closely with that required by theory. A similar interaction occurs with the hydrocarbons, toluene, ethylbenzene, the three xylenes, cumene, ψ -cumene, mesitylene, and cymene, which are all solvents for mercuric chloride; carbon disulphide and the hydrocarbons, hexane and decane, which do not dissolve mercuric chloride, fail to bring about an interaction between aluminium and mercuric chloride. W. A. D.

Haloid Substitution in some Nitro-Halogenated Substances.

JAN J. BLANKSMA (*Rec. trav. chim.*, 1904, 23, 125—130).—When *s*-dibromotoluene is slowly added to four times its weight of nitric acid of sp. gr. 1.52 and the mixture warmed for 10 minutes at 100° , there is formed a product crystallising in cubes and melting at 106 — 108° (already obtained by Neville and Winther, *Trans.*, 1880, 37, 431, in addition to 3:5-dibromo-2:4-dinitrotoluene, which crystallises in needles and melts at 157°). The latter reacts with ammonia and amines less readily than 1:3-dibromo-4:6-dinitrobenzene, but when dissolved in alcohol and heated with appropriate amines in closed tubes at 150° , the following substances are formed: 2:4-dinitro-3:5-diaminotoluene, yellow crystals melting at 199° ; 2:4-dinitro-3:5-di-methylaminotoluene, bright red crystals melting at 140° , and 2:4-dinitro-3:5-dianilinotoluene, red crystals melting at 162° . The product melting at 106 — 108° appears to be a mixture of 3:5-dibromo-2:4-dinitrotoluene with an isomeride.

3:5-Dibromo-2:4:6-trinitrotoluene, prepared by nitrating dibromotoluene in presence of sulphuric acid, reacts readily with ammonia and amines. 2:4:6-Trinitro-3:5-di-methylaminotoluene, so prepared, forms red crystals, melts at 156° , and, with nitric acid of sp. gr. 1.52, is converted into 2:4:6-trinitro-3:5-di-methylnitroaminotoluene, which may also be obtained by nitrating the dinitrodi-methylaminotoluene already described; it forms colourless crystals and melts and decomposes at 199 — 200° . 2:4:6-Trinitro-3:5-dianilinotoluene forms pale red crystals and melts at 206° ; the corresponding *toluidine* derivative is also red and melts at 185° .

When the 3:5-dibromo-2:4:6-trinitrotoluene or 3:5-dibromo-2:4-dinitrotoluene is treated with sodium methoxide, only resinous products are formed, due apparently to the oxidation of the methyl group by the nitro-group in the *ortho*-position, since 2:4:6-tribromo-3:5-dinitrotoluene, although the reactivity of its bromine atoms is diminished by the presence of the methyl group, furnishes, with sodium methoxide and methyl alcohol at 100° a crystalline product composed of a mixture of a mono- with a dibromo-derivative.

s-Tribromodinitrobenzene, prepared by Loring Jackson's method, reacts with methylamine to form 2:4-dinitro-1:3:5-trimethylaminobenzene, which forms orange-red crystals, melts at 220° , and is

converted by nitric acid into *s-trinitrotri-methylnitroaminobenzene*, which is colourless, crystallises from acetic acid and explodes at 200—203°, occasionally bursting into flame simultaneously. T. A. H.

Preparation of Salts of Sulphamic Acids of Benzene and its Homologues. HUGO WEIL (D.R.-P. 151134).—Nitrobenzene and its homologues are readily reduced by solutions of hydrogen sulphites, the principal products being sulphamates, together with small quantities of aminosulphonates, the yield of the former increasing with the number of alkyl groups in the benzene ring. The reaction proceeds according to the equation: $\text{ArNO}_2 + 3\text{NaHSO}_3 = \text{NHAr}\cdot\text{SO}_3\text{Na} + 2\text{NaHSO}_4$, or, when neutral sulphite is added $\text{ArNO}_2 + \text{NaHSO}_3 + 2\text{Na}_2\text{SO}_3 = \text{NHAr}\cdot\text{SO}_3\text{Na} + 2\text{Na}_2\text{SO}_4$. In practice, calcium hydrogen sulphite is the most convenient reagent. The reaction only takes place in dilute solution, and this is perhaps the reason why it has hitherto been overlooked. The alkali sulphamates are precipitated from their solutions by the addition of sodium chloride, and when recrystallised from 95 per cent. alcohol, form well-developed crystals.

The sulphamic acids derived from *p*-toluidine and the xylydines may be precipitated from solutions of their sodium salts by dilute hydrochloric acid. Their melting points vary according to the rate of heating. Boiling dilute acids readily hydrolyse them to aminosulphonic acids. C. H. D.

Preparation of Alkylsulphinic Acids. ARTHUR ROSENHEIM and LUDWIG SINGER (*Ber.*, 1904, 37, 2152—2154).—The following acids were prepared by the action of sulphur dioxide on ethereal solutions of magnesium alkyl haloids.

Magnesium ethylsulphinate crystallises in glistening, colourless flakes, *magnesium propylsulphinate* in colourless plates, *magnesium benzenesulphinate*, $2\text{Mg}(\text{PhSO}_2)_2\cdot\text{PhSO}_2\cdot 6\text{H}_2\text{O}$, as a microcrystalline powder, and the normal *sodium* and *silver* benzenesulphinates in colourless plates and needles respectively, whilst benzenesulphinic acid forms stellar aggregates of colourless prisms melting at 84°. *o*-Toluenesulphinic acid and naphthalene- α -sulphinic acid can be obtained in a similar manner. E. F. A.

Styrenes. VI. AUGUST KLAGES (*Ber.*, 1904, 37, 2301—2317. Compare Abstr., 1902, i, 611, 666; 1903, i, 19; this vol., i, 302, 497).—The term “styrolene” is introduced by the author to designate those styrenes which possess an additional double linking in the side-chain; a “styrodienene” possesses two double linkings in the side-chain, and a “styrotriene” three. The present communication deals mainly with $\Delta^{1,2}$ - and $\Delta^{1,3}$ -styrolenes.

α -Dimethyl- $\Delta^{2,3}$ -butadienyl-benzene (phenyltrimethylallene),
 $\text{CMePh}\cdot\text{C}:\text{CMe}_2$,

prepared from mesityl oxide and magnesium phenyl bromide, is a strongly refracting oil with an odour of lemons and boils at 107—108° under 20 mm. pressure, has a sp. gr. 0.9277 at 19.8°/4° and n_D 1.5236. The tertiary alcohol, resulting as the primary product of the Grignard reaction in question, appears to lose water with great ease. When

oxidised either by potassium permanganate and sulphuric acid or by chromic acid, phenyltrimethylallene forms acetophenone, which was identified by its phenylhydrazone and its semicarbazone. *Phenyltrimethylallene tetrabromide*, prepared by the action of bromine on the hydrocarbon at 0° , is an inodorous syrup. When the hydrocarbon is reduced by sodium and alcohol, it forms α -dimethyl- Δ -butenylbenzene, $\text{CHMePh}\cdot\text{CH}\cdot\text{CMe}_2$, a colourless liquid with an odour of geranium; it boils at $98\text{--}100^\circ$ under 19 mm. pressure and at $210\text{--}211^\circ$ under 755 mm. pressure, has a sp. gr. 0.8931 at $20^\circ/4^\circ$ and n_D 1.5162; its *nitrosylchloride* melts at 140° . In order to prove that, during its formation from trimethoxyphenylallene, the addition of hydrogen occurred at the Δ^α - and not at the Δ^β -position, where the double linking is retained, the compound, which would have been formed had the addition of hydrogen occurred at the Δ^β -position and where the double linking in the Δ^α -position is retained, was prepared by the action of magnesium isobutyl iodide on acetophenone, namely, α -dimethyl- Δ^α -butenylbenzene, $\text{CMePh}\cdot\text{CH}\cdot\text{CHMe}_2$; it is a mobile oil and boils at $99\text{--}101^\circ$ under 20 mm. pressure, has a sp. gr. 0.8498 at $15^\circ/4^\circ$ and n_D 1.516; that this compound was actually a Δ^α -hexenylbenzene was proved by its conversion during reduction into *sec-hexenylbenzene* [α -dimethylbutylbenzene], $\text{CHMePh}\cdot\text{CH}_2\cdot\text{CHMe}_2$, a mobile oil, boiling at 77° under 9 mm. pressure, having a sp. gr. 0.8634 at $15^\circ/4^\circ$ and n_D 1.4876, and forming crystalline *barium, sodium, magnesium, and copper sulphonates*.

From the action of magnesium isobutyl iodide on acetophenone, the primary product *dimethobutylolbenzene* [α -hydroxy- α -dimethylbutylbenzene], $\text{CMePh}(\text{OH})\cdot\text{CH}_2\cdot\text{CHMe}_2$, was isolated; it is a syrupy, almost inodorous oil, and boils at $110\text{--}112^\circ$ under 12 mm. pressure.

1-Phenyl- $\Delta^{\alpha\gamma}$ -butadiene, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2$, the preparation of which from styrylmethylcarbinol has previously been described by the author, may also be prepared by the action of an excess of magnesium methyl iodide on cinnamaldehyde (compare von der Heide, this vol., i, 583). When reduced by sodium and alcohol, it forms α -phenyl- Δ^β -butylene (Δ^β -butenylbenzene), $\text{CH}_2\text{Ph}\cdot\text{CH}\cdot\text{CHMe}$, a mobile oil which boils at 176° under 765 mm. and at 76° under 18 mm. pressure, and has a sp. gr. 0.8857 at $15^\circ/4^\circ$ and n_D 1.5109 at 15° . Its constitution was established by its forming phenylacetaldehyde when oxidised by ozone (Harries). When heated with alcoholic potassium hydroxide at $160\text{--}180^\circ$, it undergoes rearrangement, the double linking shifting from the Δ^β - to the Δ^α -position; phenyl- Δ^α -butylene dibromide was isolated. α -Phenyl- Δ^α -butylene, $\text{CHPh}\cdot\text{CHEt}$, was then reduced to *n*-butylbenzene.

Phenylpropylcarbinol, $\text{CHPrPh}\cdot\text{OH}$, prepared by the action of magnesium propyl iodide on benzaldehyde, is a colourless oil which has a sp. gr. 1.0212 at $18^\circ/4^\circ$, and boils at 110° under 15 mm. pressure. When its *chloride*, which is a colourless oil, boiling and decomposing at 94° under 20 mm. pressure, is heated with pyridine at 125° , α -phenyl- Δ^α -butylene (Δ^α -butenylbenzene), $\text{CHPh}\cdot\text{CHEt}$, is formed; it boils at $89\text{--}90^\circ$ under 15 mm. and at 189° at the ordinary pressure, and has a sp. gr. 0.9124 at $16^\circ/4^\circ$ and n_D 1.5414. It accordingly possesses a higher specific gravity, a higher boiling point and a higher molecular refraction than its isomeride of the Δ^β -series.

γ-Hydroxybutylbenzene, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$, prepared by the reduction of benzylacetone with sodium and alcohol, boils at $236\text{--}238^\circ$, has a sp. gr. 0.9899 at $16.5^\circ/4^\circ$, and n_D 1.517 at 16.5° ; its *phenylurethane* separates from alcohol in colourless needles and melts at 113° .

γ-Hydroxy-γ-methylbutylbenzene, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{OH}$, prepared by the action of magnesium methyl iodide on benzylacetone, boils at 121° under 13 mm. pressure; its *phenylurethane* separates from alcohol in glistening needles and melts at $143\text{--}144^\circ$. By the action of hydrochloric acid and pyridine, it is converted into α -phenyl- γ -methyl- Δ^β -butylene, $\text{CH}_2\text{Ph}\cdot\text{CH}\cdot\text{CMe}_2$, which boils at 92° under 15 mm. and at 205° under the ordinary pressure. That this product was identical with the ametylbenzene previously described by the author was shown by the identity of the dibromides and nitroschlorides prepared from the respective styrenes, which moreover were identical in physical properties and yielded the same α -phenyl- γ -methyl- Δ^α -butylene when boiled with alcoholic potassium hydroxide: in both cases, the same products are formed when oxidation by ozone is effected (Harries), thus: $\text{CH}_2\text{Ph}\cdot\text{CH}\cdot\text{CMe}_2 \rightarrow \text{Ph}\cdot\text{CH}_2\cdot\text{CHO} + \text{COMe}_2$. The transformation of α -phenyl- γ -methyl- Δ^β -butylene into the isomeric Δ^α -compound takes place slowly at 180° under the influence of alcoholic potassium hydroxide. The Δ^α -styrene, in contradistinction to the Δ^β -isomeride, which is not capable of being reduced, is converted by sodium and alcohol into *isoamylbenzene*.

Phenyl-isobutylcarbinol, $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CHMe}_2$, boils at 126° under 21 mm. pressure, and has a sp. gr. 0.9567 at $17^\circ/4^\circ$; when its chloride is heated with pyridine, it forms α -phenyl- γ -methyl- Δ^α -butylene, $\text{CHPh}\cdot\text{CH}\cdot\text{CHMe}_2$, which boils at $102\text{--}103^\circ$ under 26 mm., at 207° under 757 mm. pressure, has a sp. gr. 0.8903 at $14.6^\circ/4^\circ$, and n_D 1.5248. The *dibromide* of the latter compound melts at 128° . When α -phenyl- γ -methyl- Δ^α -butylene is reduced, it forms *isoamylbenzene*, boiling at $198\text{--}199^\circ$ under 757 mm. pressure.

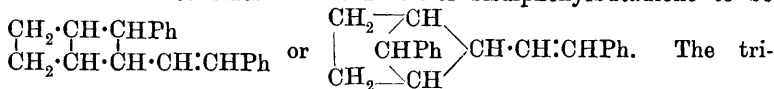
γ-Hydroxy-γ-methylamylbenzene, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{C}(\text{OH})\text{MeEt}$, prepared by the action of magnesium ethyl iodide on benzylacetone, boils at $129\text{--}130^\circ$ under 13 mm. pressure and has a sp. gr. 0.9690 at $15.3^\circ/4^\circ$. Its *phenylurethane* melts at $94\text{--}95^\circ$. When the chloride of the carbinol just described is heated with pyridine at 125° , α -phenyl- γ -methyl- Δ^β -pentene, $\text{CH}_2\text{Ph}\cdot\text{CH}\cdot\text{CMeEt}$, is formed; this boils at $103\text{--}104^\circ$ under 15 mm. and at 226° under 749 mm. pressure, has a sp. gr. 0.9004 at $18^\circ/4^\circ$ and n_D 1.5100 at 18° , and cannot be reduced by sodium and alcohol. Its *nitroschloride* separates from alcohol in glistening needles and melts and decomposes at $140\text{--}141^\circ$. A. McK.

Bisdiphenylbutadiene. C. N. RIIBER (*Ber.*, 1904, 37, 2272—2276. Compare Liebermann and Riiber, *Abstr.*, 1902, i, 669; Doebner and Staudinger, this vol., i, 149).—Oxidation of bisdiphenylbutadiene with potassium permanganate in acetone solution at $20\text{--}25^\circ$ leads to the formation of benzoic acid and a *tribasic acid*, $\text{C}_{13}\text{H}_{12}\text{O}_6$. This tribasic acid crystallises in needles, melts and effervesces at 184° , and is soluble in acetone, but only slightly so in other solvents. When distilled under 3 mm. pressure, it yields a gelatinous anhydride (?) which is

soluble in ether. The *methyl* ester distils at 200° under 0.3 mm. pressure. When heated with potassium permanganate in sulphuric acid solution, the acid is oxidised with formation of benzoic acid.

With bromine in carbon disulphide solution, bisdiphenylbutadiene forms a *tribromo*-derivative, $C_{20}H_{19}Br_3$, which melts and decomposes at 223° . It is easily soluble in boiling benzene or chloroform, but only slightly soluble in other solvents. It is not oxidised by potassium permanganate in acetone solution.

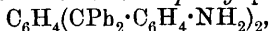
The author considers the structure of bisdiphenylbutadiene to be



The tri-
basic acid would be $\text{CO}_2\text{H} \cdot \text{CH} \text{---} \text{CH} \cdot \text{CO}_2\text{H}$

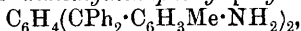
G. Y.

Derivatives of Hexaphenyl-*p*-xylene. FRITZ ULLMAN and CARL SCHLAEPFER (*Ber.*, 1904, 37, 2001—2008).—*Tetraphenyl-p-xylene glycol*, $C_6H_4(CPh_2 \cdot OH)_2$, prepared by the action of magnesium phenyl bromide on methyl terephthalate in ethereal solution, separates from benzene as a crystalline powder and melts at 169° ; in boiling benzene solution, it is converted by gaseous hydrogen chloride into *tetraphenyl-p-xylene chloride*, $C_6H_4(CPh_2Cl)_2$, which melts at 247° and interacts with aniline, giving *dianilinetetraphenyl-p-xylene*, $C_6H_4(CPh_2 \cdot NHPh)_2$. This substance crystallises from benzene in white leaflets and melts at 225° . The isomeric 4':4'-*diaminohexaphenyl-p-xylene*,



is formed when tetraphenyl-*p*-xylene glycol is heated with aniline hydrochloride and glacial acetic acid; it forms an indistinctly crystalline powder, melts at 358° , and is sparingly soluble in most solvents; the *dihydrochloride*, $C_{44}H_{38}N_2Cl_2$, melts at 355° , and the *diacetyl* derivative, $C_{48}H_{40}O_2N_2$, crystallises from xylene and melts at 231° .

4':4'-*Diamino-3':3'-dimethylhexaphenyl-p-xylene*,



prepared from tetraphenyl-*p*-xylene glycol and *o*-toluidine hydrochloride, crystallises from xylene and melts at 277° ; the *dihydrochloride* melts at 259° . 4':4'-*Dimethylamino-3':3'-dimethylhexaphenyl-p-xylene*, $C_6H_4(CPh_2 \cdot C_6H_3Me \cdot NHMe)_2$, obtained by using methyl-*o*-toluidine, forms a white, crystalline powder and melts at 287° .

Tetraphenyl-p-xylene, $C_6H_4(CHPh_2)_2$, prepared by reducing tetraphenyl-*p*-xylene glycol with zinc dust and glacial acetic acid, crystallises from the acid in white needles and melts at 172° .

4':4'-*Dihydroxyhexaphenyl-p-xylene*, $C_6H_4(CPh_2 \cdot C_6H_4 \cdot OH)_2$, prepared by adding concentrated sulphuric acid to a mixture of phenol and tetraphenyl-*p*-xylene glycol in glacial acetic acid, crystallises in small colourless prisms and melts at 304° . A similar condensation with salicylic acid could not be effected.

W. A. D.

Formation of Chloroanilines. EYVIND BOEDTKER (*Compt. rend.*, 1904, 1174—1175).—*p*-Chloroaniline is sometimes formed during the

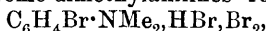
reduction of nitrobenzene with tin and hydrochloric acid. The reaction is expressed by the equation : $\text{C}_6\text{H}_5\cdot\text{NO}_2 + \text{HCl} + 2\text{H}_2 = \text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2 + 2\text{H}_2\text{O}$.
S. S.

Action of Bromine on the Salts of Aromatic Amines with Halogen Hydrides. K. FRIES (*Ber.*, 1904, 37, 2338—2346).—The primary products resulting from the action of bromine on the salts of aromatic amines with halogen hydrides are additive compounds, the transformation of which into substitution derivatives takes place with ease in the cases of compounds of primary and secondary amines. The perbromides of tertiary amines, where the para- and ortho-positions relatively to the amino-group are free, exhibit considerable tendency to transformation into substitution products; where the para-position, however, is substituted, the compounds in question are very stable.

p-Bromodimethylaniline hydrobromide perbromide,

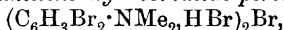


prepared from *p*-bromodimethylaniline hydrobromide (2 mols.) and bromine (1 mol.), crystallises from glacial acetic acid in long, dark red prisms, which soften at 95° and melt at 107°. *p*-Bromodimethylaniline is formed by the action of acetone or sodium hydrogen sulphite on this compound, whilst with sodium acetate a mixture of equal parts of monobromo- and dibromo-dimethylanilines results. The compound,



prepared from *p*-bromodimethylaniline hydrobromide (1 mol.) and bromine (1 mol.), separates from glacial acetic acid in dark red plates and melts at 70—75°. It behaves towards acetone, sodium hydrogen sulphite, and sodium acetate like the compound first described. Water converts it into dibromodimethylaniline and tetramethylbenzidine hydrobromide perbromide, $\text{C}_{12}\text{H}_8(\text{NMe}_2)_2, 2\text{HBr}, \text{Br}_4$; the latter melts at about 158° with evolution of hydrogen bromide; with sodium hydrogen sulphite, it forms tetramethylbenzidine.

o-*p*-Dibromodimethylaniline hydrobromide perbromide,



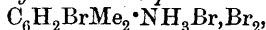
prepared from dibromodimethylaniline hydrobromide and bromine in glacial acetic acid solution, forms plates with a greenish-black lustre and melts and decomposes at 135°. The compound



prepared from *o*-*p*-dibromodimethylaniline hydrobromide (1 mol.) and bromine (1 mol.), crystallises in prisms and melts at 102°.

as-*m*-Xylidine hydrobromide perbromide, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{NH}_3\text{Br}, \text{Br}_2$, forms bromo-xylidine when acted on by water; it readily parts with bromine at the ordinary temperature, xylidine hydrobromide being left.

Bromo-as-*m*-xylidine hydrobromide perbromide,



forms red plates and melts and decomposes at 134°. On exposure to air, bromine is separated and bromoxylidine hydrobromide regenerated.

o-*p*-Dibromomethylaniline hydrobromide perbromide,



forms yellowish-red, triclinic pyramids and melts and decomposes at 125°. It is comparatively stable and parts with bromine only after several days' exposure to air; it may be recrystallised from glacial

acetic acid containing a little hydrobromic acid. When its solution in glacial acetic acid is warmed, a mixture of dibromo- and tribromo-methylanilines is produced.

A. McK.

Action of Phosphorus Trichloride on some Primary Cyclic Amines at the Boiling Point; Reduction of Phosphorus Trichloride with Formation of Phosphorus. PAUL LEMOULT (*Compt. rend.*, 1904, 138, 1223—1225. Compare Abstr., 1903, i, 672; this vol., i, 380).—The action of phosphorus trichloride on cyclic amines has been studied by Jackson and Mencke (Abstr., 1885, 254), and by Hinzberg (Abstr., 1894, i, 580), who found that in addition to the arylamides of phosphoric acid, hydrogen phosphide and a red amorphous substance, probably red phosphorus, were also formed. The author, however, finds that when 1 mol. of phosphorus trichloride is gradually added to 8 mols. of aniline dissolved in benzene, ether, or chloroform there is a vigorous action, and aniline hydrochloride is formed; on distilling off the solvent and heating the residual liquid to boiling for several days, an orange-red solid is deposited, and there is a strong odour of phosphorus, but no gas is evolved. The residual solid consists of diphenylamine, the anilide of phosphoric acid, $\text{PO}(\text{NPh})_3$, the compound $\text{PCl}(\text{NPh})_4$, and an insoluble red substance containing 85 per cent. of phosphorus; if the heating be discontinued directly the red solid begins to separate, white phosphorus can be extracted by means of carbon disulphide from the mixture. With the exception of the diphenylamine, the crystalline products are the same as those obtained by the action of phosphorus pentachloride on aniline, and it is probable therefore that the phosphorus trichloride is converted into the pentachloride and free phosphorus according to the equation $5\text{PCl}_3 = 3\text{PCl}_5 + \text{P}_2$. Similar series of compounds are obtained when methylaniline, *o*- or *p*-toluidine, or xylydine are used instead of aniline.

M. A. W.

Preparation of Phenylaminoacetonitrile. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 151538).—Phenylaminoacetonitrile, $\text{NPh}\cdot\text{CH}_2\cdot\text{CN}$, was obtained by Miller and Plöchl (Abstr., 1892, 1189) by the action of dry hydrogen cyanide on anhydro-formaldehydeaniline, $\text{C}_6\text{H}_5\cdot\text{N}:\text{CH}_2$. It is more conveniently prepared by mixing aniline, formaldehyde, potassium cyanide, and a mineral acid in molecular proportion in aqueous or alcoholic solution.

C. H. D.

Piria's Thionaphthamic Acid and the Products of the Action of Aminosulphonic Acid on α -Naphthylamine. Preparation of α -Aminonaphthalene-2-sulphonic Acid. J. C. RUIJTER DE WILDT (*Rec. trav. chim.*, 1904, 23, 173—186).—The author confirms the statement of Piria (*Annalen*, 1851, 73, 54) that when α -nitronaphthalene, dissolved in alcohol, is treated with an aqueous solution of sodium sulphite, α -naphthylsulphamic acid is produced. He has also repeated the experiments of Paal and Jaenecke (Abstr., 1896, i, 235), and finds that when α -naphthylamine is treated with

amidosulphonic acid by the method recommended by these authors the principal product is a mixture of the 1:2- and 1:4-naphthylamine-sulphonic acids, and not, as they assert, a stable α -naphthylsulphamic acid. The 1:2-naphthylaminesulphonic acid was separated from the mixture by precipitation as the barium salt (which forms brilliant, white scales) and regeneration from this. It crystallises in long needles and melts and decomposes at $262-265^\circ$ (compare Erdmann, Abstr., 1893, i, 653 and 655). When the silver salt is heated in closed tubes at 100° with ethyl iodide, 1-ethylaminonaphthalene-2-sulphonic acid is formed; this crystallises from water in needles and melts at $207-208^\circ$. It is soluble in strong acids and is reprecipitated from its solution in hydrochloric acid on addition of water. The potassium, barium, lead, and silver salts are very soluble in water.

Piria's acid may, however, be obtained by mixing aminosulphonic acid with α -naphthylamine and warming the mixture to $85-95^\circ$, when a slight turbidity appears. If the heating is then discontinued, the temperature rises spontaneously to $100-113^\circ$ and the liquid solidifies. From the mass, the acid may be obtained by washing first with a mixture of ether and benzene, then with ether alone, and finally converting into the potassium salt. The acid may also be obtained by the action of chlorosulphonic acid on α -naphthylamine dissolved in chloroform or carbon tetrachloride.

T. A. H.

Oxygen Ethers of Carbamide. W. M. BRUCE (*J. Amer. Chem. Soc.*, 1904, 26, 449-464. Compare this vol., i, 491).—*O-Methyl diphenyldiureidoisocarbamide*, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}(\text{OMe})\cdot\text{N}\cdot\text{CO}\cdot\text{NHPh}$, prepared from methyl phenylisobiuret and phenylcarbimide, melts at 153° . When treated with dry hydrogen chloride at 60° , it forms *carbonyl diphenyldicarbamide*, $(\text{NHPhCO}\cdot\text{NH})_2\text{CO}$, which melts at 211° . *O-Methyl carbethoxyisocarbamide*, $\text{OEt}\cdot\text{CO}\cdot\text{N}\cdot\text{C}(\text{OMe})\cdot\text{NH}_2$, prepared from methyl isocarbamide hydrochloride, potassium hydroxide, and ethyl chlorocarbonate, melts at 5° . When hydrogen chloride is passed into the dry ethereal solution of the preceding compound, ethyl allophanate is formed, *O-methyl carbethoxyisocarbamide* hydrochloride readily parting with methyl chloride.

O-Methyl thiophenyldiureidoisocarbamide, $\text{NHPh}\cdot\text{CS}\cdot\text{N}\cdot\text{C}(\text{OMe})\cdot\text{NH}_2$, prepared from methyl isocarbamide and phenylcarbimide, separates from benzene in diamond-shaped plates and melts at 131° . *O-Methyl isobiuret*, $\text{NH}_2\cdot\text{CO}\cdot\text{N}\cdot\text{C}(\text{OMe})\cdot\text{NH}_2$, prepared from methyl isocarbamide hydrochloride and potassium isocyanate, melts at 118° . When treated with dry hydrogen chloride, methyl chloride is evolved and biuret produced.

Benzylidenedimethyldiisocarbamide, $\cdot\text{CHPh}[\text{NH}\cdot\text{C}(\text{OMe})\cdot\text{NH}]_2$, formed from methyl isocarbamide and benzaldehyde, melts at 137° ; small quantities of tribenzylidenetetraisocarbamide are also formed. When benzylidenedimethyldiisocarbamide is treated with dry hydrogen chloride, benzylidenediureide is produced. *Benzylidenediethyldiisocarbamide*, $\text{CHPh}:[\text{NHC}(\text{OEt})\cdot\text{NH}]_2$, prepared from ethyl isocarbamide and benzaldehyde, melts at 154° .

By condensation of isocarbamide ethers with esters of β -ketonic acids, oxygen ethers of 2-hydroxypyrimidines are readily formed

6-Hydroxy-2-methoxy-4-methylpyrimidine, $\text{N} \begin{smallmatrix} \text{C(OMe)-N} \\ \text{C(OH):CH} \end{smallmatrix} \text{CMe}$, prepared from methyl isocarbamide and ethyl acetoacetate, separates from alcohol in feathery masses of needles and melts at 207° . Its hydrochloride readily evolves methyl chloride with the formation of methyluracil. 6-Hydroxy-2-ethoxy-4-methylpyrimidine separates from ethyl alcohol in shining needles and melts at 206° . 6-Hydroxy-2-methoxy-4-methyl-5-ethylpyrimidine, prepared from methyl isocarbamide and ethyl acetoacetate, separates from ethyl alcohol in needles and melts at 210° . O-Methyl oxalylisocarbamide (μ -methyl parabanic acid), $\text{OMe} \cdot \text{C} \begin{smallmatrix} \text{N} \cdot \text{CO} \\ \text{NH} \end{smallmatrix} \text{CO}$, prepared from methyl isocarbamide and ethyl oxalate, separates from ethyl alcohol in three-sided prisms and melts at 137.5° . Its hydrochloride readily decomposes to form oxalylurea.

The affinity constants of various isocarbamides were determined. With methyl isocarbamide, there is practically no hydrolysis where $v = 1024$; the molecular conductivity at infinite dilution = 239.6 . The results, obtained with methyl isocarbamide, are contrasted with those obtained by Walker for carbamide. Methyl isocarbamide is a stronger base than carbamide, its affinity constant being 6.4×10^{-5} , a value of the same order as that of ammonia. The molecular conductivity of ethyl isocarbamide at infinite dilution is 234.6 . Ethyl isocarbamide is nearly twice as strong a base as methyl isocarbamide. The substitution of an ethyl for a methyl group attached to oxygen causes a much more decided increase in the affinity constant than is the case when a similar single substitution is effected for a methyl group attached to nitrogen. The molecular conductivity of methyl phenylisocarbamide at infinite dilution is 225.5 ; the affinity constant of methyl phenylisocarbamide is $1/300$ that of methyl isocarbamide. The molecular conductivity of ethyl phenylisocarbamide at infinite dilution is 224.2 ; the substitution of the ethyl for the methyl group doubles the strength of the base.

A. McK.

Constitution of Aromatic Purpuric Acids. V. The Purpurate Reaction with 2:4-Dinitrophenols. WALTHER BORSCHKE and E. BÖCKER (*Ber.*, 1904, 37, 1843—1853. Compare this vol., i, 166).—Purpurate formation does not take place with mononitrophenols and potassium cyanide. At least two nitro-groupings must be present in the phenol molecule; those must be in the meta-position to one another, and at least one of them must be contiguous to the phenolic hydroxyl group. Purpurates are accordingly sharply differentiated into two classes, according as they are derived from 2:4- or 2:6-dinitrophenols. The present research deals with purpurate formation from 2:4-dinitrophenols.

Potassium metapurpurate (potassium 4-nitro-2-hydroxylamino-3-cyanophenoxide) was prepared by the reduction of 2:4-dinitrophenol with potassium cyanide in aqueous solution; in alcoholic solution, considerable quantity of potassium 2:4-dinitro-3-cyanophenoxide is formed. The addition of hydrogen cyanide in those reactions is

discussed with reference to Thiele's theory of conjugated double-linking.

Ammonium metapurpurate, prepared by decomposing potassium metapurpurate by phosphoric acid and then adding an ethereal solution of ammonia to the ethereal solution of the liberated metapurpuric acid, is at first a red, amorphous mass, which gradually becomes crystalline. When barium chloride is added to its aqueous solution, *barium metapurpurate* separates in dark red, glistening needles. The free acid (4-nitro-2-hydroxylamino-3-cyanophenol), prepared by cooling ammonium metapurpurate in aqueous solution to 0° and adding the calculated amount of phosphoric acid, is a dark red powder, which decomposes at 92° with evolution of nitric oxide. When quite dry, it is stable; it is decomposed by moisture, although it may be preserved unchanged for days in presence of an excess of water; its ethereal is much more stable than its aqueous solution.

Potassium o-cresolpurpurate (potassium 5-nitro-3-hydroxylamino-4-cyano-2-hydroxy-1-methylbenzene), prepared from dinitro-*o*-cresol and potassium cyanide in aqueous solution, yields the corresponding ammonium salt, from which *o-cresolpurpuric acid* is readily formed; the latter, when absolutely dry, is a stable, dark reddish-violet powder, and decomposes at 180° with evolution of nitric oxide.

The *potassium salt of ethyl 5-nitro-3-hydroxylamino-4-cyano-2-hydroxybenzoate*, prepared by the action of potassium cyanide on ethyl dinitrosalicylate, crystallises from water in brick-red needles; the corresponding ammonium salt was also prepared. *Ethyl 5-nitro-3-hydroxylamino-4-cyano-2-hydroxybenzoate*, prepared by decomposing the potassium salt with phosphoric acid, first forms an amorphous, orange-yellow powder, which crystallises from glacial acetic acid in blood-red needles or scales, and melts and begins to decompose at 186°.

A. McK.

Molecular Rearrangement of Aminophenyl Alkyl Carbonates. JULIUS STIEGLITZ and HENRY T. UPSON (*Amer. Chem. J.*, 1904, 31, 458—502).—It has been shown by Ransom (*Abstr.*, 1900, i, 218) that *o*-aminophenyl ethyl carbonate, formed by the reduction of *o*-nitrophenyl ethyl carbonate with tin and hydrochloric acid, undergoes molecular rearrangement with formation of hydroxyphenylurethane. The present investigation was undertaken with the object of ascertaining the degree to which the tendency to suffer rearrangement exists in the substitution products of *o*-aminophenyl ethyl carbonate and the extent to which the amines or their salts can be isolated as intermediate products, and also to determine the velocity with which the rearrangement takes place and the factors on which it depends.

The results show that each of the *o*-aminophenyl carbonates studied exhibits a tendency to change into its corresponding urethane, and in every case the hydrochloride of an amine can be isolated. A detailed account of this portion of the work is reserved for a future paper.

The following affinity constants, *K* aff., and velocity constants of rearrangement, *k*, were found by determining the conductivity of

solutions of the hydrochlorides at 0°, according to Stieglitz and Derby's method (this vol., ii, 464).

| | <i>K</i> . | <i>K</i> aff. $\times 10^{14}$. | <i>k</i> . |
|---|------------|----------------------------------|------------|
| 4-Aminophenyl methyl carbonate..... | 23200 | 27800 | — |
| 4-Aminophenyl ethyl carbonate | 22050 | 26500 | — |
| 2-Aminophenyl methyl carbonate..... | 1040 | 1250 | 0.1017 |
| 2-Aminophenyl ethyl carbonate | 800 | 960 | 0.0578 |
| 2-Amino-4-methylphenyl ethyl carbonate .. | 1020 | 1225 | 0.0186 |
| 2-Amino-5-methylphenyl ethyl carbonate... | 1800 | 2160 | 0.0717 |
| 2-Amino-6-methylphenyl ethyl carbonate... | 880 | 1050 | 0.0659 |

(*K* signifies that the affinity constant of the base is $K \times$ the degree of dissociation of water, 1.2×10^{-14} ; K aff. = $K \times 1.2 \times 10^{-14}$.)

These results lead to the following conclusions: the *o*-aminophenyl alkyl carbonates are very much weaker bases than the corresponding para-derivatives. 2-Amino-5-methylphenyl ethyl carbonate, containing the methyl group in the *p*-position to the amino-group, is decidedly stronger than the isomeric bases in which the methyl group occupies the *m*-position to the amino-group. The velocity constants indicate that the rearrangement depends entirely on the presence of the free base in solution, that the free acid retards the rearrangement by forming the salt, and that the actual rate of the change is the result of two simultaneous reactions, one a non-reversible reaction of rearrangement of the free base, and the other a reversible reaction which results in a condition of equilibrium between the salt, water, the free acid, and the free base. The velocity constants appear to depend mainly on changes affecting the substituted carboxyl group, and but little on the more or less positive nature of the amino-group; the base containing the methyl-substituted carboxyl group undergoes rearrangement nearly twice as rapidly as the corresponding base containing the ethyl group. The velocity constant is considerably reduced by the substitution of methyl for hydrogen in the para-position to the carboxyl group.

The behaviour of the hydrochlorides of the following halogen derivatives has been studied.

4-Chloro-2-aminophenyl ethyl carbonate, 6-chloro-2-aminophenyl ethyl carbonate, 4-bromo-2-aminophenyl ethyl carbonate, 6-bromo-2-amino-4-methylphenyl ethyl carbonate, 4-bromo-2-amino-6-methylphenyl ethyl carbonate, 4:6-dichloro-2-aminophenyl ethyl carbonate, and 4-chloro-6-bromo-2-aminophenyl ethyl carbonate. The velocity of rearrangement has been determined in *N*/32 solution at 25° and compared with that of the corresponding unsubstituted compounds. The results obtained lead to the following conclusions. The methyl group in the 4-position retards the rearrangement both at 25° and at 0°, whilst in the 6-position it delays the rearrangement somewhat at 25°, but accelerates it slightly at 0°. A halogen atom in the 6-position causes a considerably increased velocity as compared with its effect in the 4-position. The substitution of a halogen atom for hydrogen in the 4-position in the amino-phenyl or -tolyl alkyl carbonates exerts a retarding effect on the velocity of the change. The rearrangement in the solutions of the salts of the halogen derivatives, as in the case of

the unsubstituted compounds, is found to be wholly dependent on the presence of the free base. E. G.

Nitration of 1-Methoxy-(ethoxy)-3-chloro-(bromo)-6-nitrobenzene. JAN J. BLANKSMA (*Rec. trav. chim.*, 1904, 23, 119—124. Compare Abstr., 1903, i, 164).—When 1-bromo-3:4-dinitrobenzene is treated with sodium methoxide dissolved in methyl alcohol, there is formed 3-bromo-6-nitroanisole, which separates from alcohol in silky needles, melts at 90°, and, with sodium methoxide in methyl alcohol, furnishes the dimethyl ether of 4-nitroresorcinol (Meldola, *Proc.*, 1901, 17, 131). When the bromonitroanisole is warmed with nitric acid of sp. gr. 1.52, there is formed 3-bromo-4:6-dinitroanisole, which crystallises in colourless spangles, melts at 110°, and is converted by sodium methoxide into the dimethyl ether of 4:6-dinitroresorcinol (Meldola, *loc. cit.*). The bromine atom in the bromodinitroanisole is mobile, and the substance furnishes, with ammonia in alcohol, the corresponding dinitroanisidine, which melts at 156°, and with methylamine the corresponding *dinitromethylaminoanisole*, a yellow, crystalline substance which melts at 198°. The analogous *ethylamine* derivative melts at 148° and the 4:6-dinitro-3-anilinoanisole occurs in yellow crystals and melts at 168°.

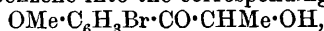
With nitric acid of sp. gr. 1.52, bromodinitroanisole furnishes 3-bromo-2:4:6-trinitroanisole, which reacts with amines like the corresponding chloro-derivative (Abstr., 1903, i, 158).

When 3-chloro-6-nitroanisole, prepared like the analogous bromo-derivative, is warmed with nitric acid of sp. gr. 1.52, 3-chloro-4:6-dinitroanisole is formed; this crystallises in colourless needles or spangles and melts at 105°. With sodium sulphide dissolved in alcohol, it is converted into *tetranitrodimethoxydiphenyl sulphide*, which forms yellow crystals melting at 204°, and with sodium disulphide into the corresponding *disulphide*, which melts and decomposes at 236°.

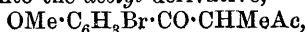
2-Chloro-4:6-dinitrophenyl ethyl ether, prepared like its lower homologue, melts at 112° and, with aniline dissolved in alcohol, furnishes 4:6-dinitro-3-anilinophenyl ethyl ether, which forms yellow crystals and melts at 170°.

These observations indicate that in the nitration of these substances, derivatives having the nitro-group in the para-position relatively to the alkyloxy-group are principally formed, the amount of ortho-derivative produced, if any, being very small. T. A. H.

Anethole. PAUL HOERING (*Ber.*, 1904, 37, 1542—1560. Compare Hell, Abstr., 1895, i, 341; 1896, i, 169; with Gärtner, Abstr., 1895, i, 341; with von Günthert, Abstr., 1896, i, 20; with Hollenberg, Abstr., 1896, i, 354).—Attempts to convert 3-bromo-4-methoxy-1-β-bromopropionylbenzene into the corresponding alcohol,

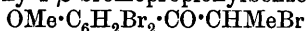


by the action of aqueous or alcoholic potassium hydroxide or barium hydroxide gave only bromoanisic acid (compare Breuninger, Diss., Erlangen); boiling alcoholic potassium acetate, on the other hand, converts the ketone into the *acetyl* derivative,



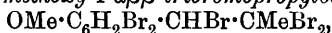
which crystallises from alcohol in colourless needles and melts at 87° ; the analogous *benzoyl* derivative, $\text{OMe}\cdot\text{C}_6\text{H}_5\cdot\text{Br}\cdot\text{CO}\cdot\text{CHMeBz}$, melts at 116° . On nitration, 3-bromo-4-methoxy-1- β -bromopropionylbenzene gives a *nitro*-derivative, $\text{C}_{10}\text{H}_9\text{O}_4\text{NBr}_2$, which crystallises from light petroleum in stellate aggregates of yellow, prismatic needles and melts at 92° .

On dissolving bromoanethole dibromide in concentrated nitric acid, 3:5-dibromo-4-methoxy-1- β -bromopropionylbenzene,



(*infra*) is obtained, which, on oxidation with chromic acid, affords 3:5-dibromoanisic acid. By fuming nitric acid of sp. gr. 1.52, on the other hand, bromoanethole dibromide is converted into 2:6-dibromo-4-nitroanisole.

3:5-Dibromoanethole dibromide is best prepared by adding anethole to a slight excess of bromine in a reflux apparatus; it crystallises from light petroleum and melts at 101.5° . With nitric acid of sp. gr. 1.48 it gives rise to 3:5-dibromo-4-methoxy-1- β -propionylbenzene, and, on oxidation with dilute nitric acid, it gives 3:5-dibromoanisic acid; 2:6-dibromo-4-nitroanisole is formed by the action of fuming nitric acid (sp. gr. 1.52). Boiling absolute methyl or ethyl alcohol do not attack dibromoanethole dibromide; boiling alcoholic sodium ethoxide, however, rapidly converts it into 3:5-dibromo-4-methoxy-1- β -bromopropylenebenzene, $\text{OMe}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}\cdot\text{CMeBr}$, which crystallises from light petroleum, melts at 58° , and combines readily with bromine to form 3:5-dibromo-4-methoxy-1- $\alpha\beta\beta$ -tribromopropylbenzene,



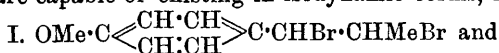
melting at 92° .

3:5-Dibromo-4-methoxy-1- β -bromopropylenebenzene is transformed by atmospheric oxygen in presence of traces of hydrogen bromide into the *ketone*, $\text{OMe}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CO}\cdot\text{CHMeBr}$, which crystallises from alcohol or light petroleum in slender needles and melts at 101° ; the ketone is remarkable for emitting during recrystallisation luminous radiations which affect a photographic plate, but are not able to discharge an electroscope (compare Armstrong and Lowry, this vol., ii, 5). On oxidation with chromic acid in acetic acid solution, 3:5-dibromo-4-methoxy-1- β -bromopropylenebenzene gives 3:5-dibromoanisic acid; by alcoholic sodium ethoxide, the olefine is not affected.

In the bromination of anethole with an excess of bromine, a *ψ*-p-dibromopropyldibromophenol, $\text{C}_9\text{H}_8\text{OBr}_4$, is always produced in varying proportions; it melts at 112 – 113° and seems to be formed from dibromoanethole dibromide by the elimination of the methyl group, as it can be obtained from this substance by heating it with hydrobromic acid for 3 hours at 120° . It has all the properties of a pseudo-bromide (Zincke, Auwers), and with lead acetate in glacial acetic acid gives at 70° an *acetyl* derivative, $\text{C}_{11}\text{H}_{11}\text{O}_3\text{Br}_3$, which crystallises from alcohol in large, six-sided plates and melts at 107 – 108° .

The author points out that whilst bromoanethole dibromide is converted by sodium ethoxide, even more readily than anethole dibromide, into a ketone, through the stages $\text{R}\cdot\text{CHBr}\cdot\text{CHMeBr} \rightarrow \text{R}\cdot\text{CH}(\text{OMe})\cdot\text{CHMeBr} \rightarrow \text{R}\cdot\text{C}(\text{OMe})\cdot\text{CHMe} \rightarrow \text{R}\cdot\text{C}(\text{OH})\cdot\text{CHMe} \rightarrow$

$R \cdot CO \cdot CH_2Me$, dibromoanethole dibromide is at once transformed into 3 : 5-dibromo-4-methoxy-1- β -bromopropylenebenzene. In order to explain this anomalous behaviour on the part of the dibromo-derivative, the author assumes that anethole dibromide and bromoanethole dibromide are capable of existing in isodynamic forms, for example :



the second of which enters into action with the alkali to give the primary methoxy-derivative, which later decomposes to form the ketone. In favour of this view are the facts that anethole and bromoanethole dibromides often solidify with difficulty, and that they readily give rise to ketones containing bromine in the benzene nucleus. Dibromoanethole dibromide, on the other hand, interacts only as if it had the structure I.

W. A. D.

Dinitrophenyl Ethers of 3-Chloro-4-aminophenol and of *p*-Aminophenol. FRÉDÉRIC REVERDIN and AUGUST DRESEL (*Ber.*, 1904, 37, 1516—1519).—3-Chloro-2' : 4'-dinitro-4-aminophenyl ether, $NH_2 \cdot C_6H_3Cl \cdot O \cdot C_6H_3(NO_2)_2$, prepared by boiling an alcoholic solution of 1-chloro-2 : 4-dinitrobenzene and 3-chloro-4-aminophenol with an excess of sodium acetate for several hours, crystallises in long, brownish-yellow needles and melts at 137°. If the alcoholic mixture is heated in absence of sodium acetate, 2-chloro-2' : 4'-dinitro-4-hydroxydiphenylamine is the sole product. When, however, 2-chloro-4-aminophenol is heated with 1-chloro-2 : 4-dinitrobenzene, either with or without the addition of sodium acetate, the principal product is always 3-chlorodinitro-4-hydroxydiphenylamine (*Abstr.*, 1903, i, 857). The position of the chlorine atom in the nucleus thus exercises a great influence on the course of the interaction. On attempting to chlorinate 3-chloro-2' : 4'-dinitro-4-aminophenyl ether with sodium chlorate and hydrochloric acid, a fission of the molecule occurs, trichloroquinone being produced.

The ether is easily diazotised, and the diazo-salt formed may be coupled with phenols to form dyes, but the products are not sufficiently resistant to alkalis to be of practical value. Satisfactory dyes, however, are obtained from the diazo-salts of 2' : 4'-dinitro-4-aminophenyl ether, $NH_2 \cdot C_6H_4 \cdot O \cdot C_6H_3(NO_2)_2$, which is obtained in the form of its *acetyl* derivative by heating an alcoholic mixture of *p*-acetylaminophenol, 1-chloro-2 : 4-dinitrobenzene, and potassium hydroxide for 2 hours; the *acetyl* compound crystallises from benzene in lustrous, yellowish-white leaflets melting at 195°, and the *base* from alcohol in dark yellow leaflets melting at 144°. In presence of sodium acetate, the base combines with 1-chloro-2 : 4-dinitrobenzene to form the diphenylamine derivative, $C_6H_3(NO_2)_2 \cdot O \cdot C_6H_4 \cdot NH \cdot C_6H_3(NO_2)_2$, melting at 225° (*D.R.-P.*, 1899, 111892).

W. A. D.

3-Amino-6-hydroxytoluene- ω -sulphonic Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (*D.R.-P.* 150313).—Sulphites react with 3-nitro-6-hydroxybenzyl chloride to form 3-nitro-6-hydroxytoluene- ω -

sulphonic acid, which is reduced by zinc dust and acid to 3-amino-6-hydroxytoluene-*o*-sulphonic acid, forming colourless needles, stable in the air, dissolving sparingly in water, readily in alkalis, and charring without melting. It is not decomposed by boiling with alkali hydroxides. The acid finds application as a photographic developer.

C. H. D.

3-Chloro-4:6-dinitrotoluene and **3-Chloro-2:4:6-trinitrotoluene**. FRÉDÉRIC REVERDIN, AUGUSTE DRESEL, and ERNEST DELÉTRA (*Bull. Soc. chim.*, 1904, [iii], 31, 631—635. Compare Abstr., 1900, i, 638).—The *acetyl* derivative of the 4'-hydroxyphenyl-4:6-dinitro-*m*-tolylamine already described (*loc. cit.*) crystallises from acetone in long, transparent needles or from benzene in reddish-brown leaflets, melts at 146—147°, and, when treated with sodium chlorate and hydrochloric acid, furnishes 4'-acetoxyphenyl-2-chloro-4:6-dinitro-3-tolylamine, which melts at 128°. When the hydroxy-compound itself is chlorinated, dichloro-derivatives analogous to those produced with dinitrohydroxydiphenylamine are formed (compare Abstr., 1903, i, 857).

When 3-chloro-4:6-dinitrotoluene dissolved in alcohol is condensed with 2-chloro-4-aminophenol in presence of sodium acetate, there is produced 3'-chloro-4'-hydroxyphenyl-4:6-dinitro *m*-tolylamine, which forms reddish-yellow, prismatic needles and melts at 176°.

3':5'-Dichloro-4'-hydroxyphenyl-4:6-dinitro-3-tolylamine, similarly prepared from the corresponding dichloroaminophenol, forms prismatic leaflets of a yellowish-green tint and melts at 230°. With anisidine, the corresponding 4'-methoxyphenyl-4:6-dinitro-*m*-tolylamine is formed; this separates from a mixture of alcohol and acetone in brilliant, brick-red prisms, and from alcohol in golden-yellow needles, which pass into the red variety immediately on warming or slowly when kept; it melts at 139°. 4'-Aminophenyl-4:6-dinitro-3-tolylamine, similarly prepared from *p*-phenylenediamine, crystallises from dilute acetone in purple-red prisms and melts at 166°.

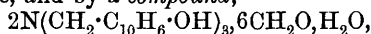
When the chlorodinitrotoluene is nitrated at 150—175° or when chlorotoluene is treated with sulphuric (66° B.) and nitric acids (49·4° B.) at 160°, 3-chloro-2:4:6-trinitrotoluene is formed; this crystallises from acetic acid in long, colourless needles, and from dilute acetone in spangles, melts at 148·5°, and is readily soluble in the usual solvents. Its solution in alcohol gives, like the chlorodinitrotoluene, a blue coloration passing rapidly into brownish-yellow with solutions of ammonia or sodium hydroxide. When warmed with ammonia in alcohol, it furnishes 2:4:6-trinitro-*m*-toluidine (Abstr., 1883, 59). With aniline, there is produced phenyl-2:4:6-trinitro-*m*-tolylamine, which crystallises from dilute acetone in golden leaflets, melts at 150°, and is soluble in chloroform, less so in ether, and slightly so in light petroleum. The corresponding derivative prepared from *p*-toluidine forms yellowish-red needles from acetic acid or dilute acetone and melts at 127°. With *p*-aminophenol, 4'-hydroxyphenyl-2:4:6-trinitro-*m*-tolylamine is formed; this crystallises from alcohol in brown scales and melts at 207°.

4'-Aminophenyl-2:4:6-trinitro-*m*-tolylamine, similarly obtained

from *p*-phenylenediamine, crystallises from dilute acetone in reddish-tinted spangles, melts at 198.5° , and is readily soluble in acetone and acetic acid, and slightly so in light petroleum and water. T. A. H.

Condensation of β -Naphthol with Formaldehyde and Ammonia. MARIO BETTI (*Gazzetta*, 1904, 34, i, 212—223. Compare *Abstr.*, 1901, i, 81, 611, 703; 1903, i, 510).—Formaldehyde differs from other aldehydes in its action on β -naphthol and an amine, with which it yields tertiary tri- β -naphtholmethyleamine bases.

Tri- β -naphtholmethyleamine, $N(CH_2 \cdot C_{10}H_6 \cdot OH)_3$, obtained by the interaction of β -naphthol, formaldehyde, and alcoholic ammonia, crystallises from ethyl acetate in long, massive needles melting at 164° . It is accompanied by a yellow substance melting at 197° , and yielding with ethyl acetate a solution exhibiting a strong, greenish-yellow fluorescence, and by a compound,



which is deposited in massive, rhombohedral crystals melting at about 158° ; the latter substance, when boiled in ethyl acetate solution, passes readily into tri- β -naphtholmethyleamine. The acetate of the latter, $N(CH_2 \cdot C_{10}H_6 \cdot OH)_3 \cdot CH_3 \cdot CO_2H$, separates from alcohol in minute, almost white plates melting at 190 — 191° . The hydrochloride separates from alcohol in shining laminae which melt and decompose at about 220° and yield the base when treated with potassium hydroxide; the benzoyl chloride derivative, $N(CH_2 \cdot C_{10}H_6 \cdot OH)_3 \cdot HCl \cdot BzCl$, crystallises from acetic acid in pale rose-coloured, stout rhombohedra, which melt and decompose at about 210° . T. H. P.

Distillation of Guaiacol with Lead Oxide. ROBERT PSCHORR and M. SILBERRACH (*Ber.*, 1904, 37, 2149—2152).—When distilled with lead oxide, guaiacol is converted into veratrole, the lead salt of guaiacol being first formed and methylated at the expense of the methyl radicle in a second molecule of guaiacol. The lead and sodium derivatives of guaiacol also give veratrole when distilled. Similarly, the lead derivative of ethyl vanilate forms veratric acid, whilst the lead derivative of resorcinol monomethyl ether yields resorcinol dimethyl ether on distillation. E. F. A.

New Reducing Agent for the Preparation of Thiophenol. W. P. WINTER (*Amer. Chem. J.*, 1904, 31, 572—577).—The method usually adopted for the preparation of thiophenol is that described by Otto (*Abstr.*, 1877, ii, 749), which consists of the reduction of benzenesulphonic chloride by means of zinc dust; this process, however, gives only about two-thirds of the theoretical yield. It is found that if the reduction is effected by the action of stannous chloride in the presence of a small quantity of zinc dust, a quantitative yield can be obtained.

E. G.

***o*-Aminobenzyl Alcohol and μ -Methylphenopentoxazole. [3-Methyl-2:4-benzoxazine.]** KARL AUWERS (*Ber.*, 1904, 37, 2249—2267).—*o*-Benzoylaminobenzyl alcohol, $NHBz \cdot C_6H_4 \cdot CH_2 \cdot OH$, formed by the action of benzoyl chloride and potassium hydrogen carbonate on

o-aminobenzyl alcohol in ethereal solution, crystallises in long, delicate, white needles and melts at 132—133° (compare Paal and Bodewig, Abstr., 1893, i, 20).

o-Aminobenzyl acetate, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{OAc}$ (Söderbaum and Widman, Abstr., 1889, 972; Gabriel and Posner, Abstr., 1895, i, 191), is formed by reduction of *o*-nitrobenzyl acetate with aluminium amalgam in ethereal solution. It is a colourless oil having an odour of aniline; the *picrate* melts at 105°. The anhydrous salts are stable towards mineral acids, but in aqueous solution are rapidly hydrolysed with formation of *o*-aminobenzyl alcohol. When warmed in ethereal solution, *o*-aminobenzyl acetate is slowly converted into *o*-acetylaminobenzyl alcohol, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{OH}$, which melts at 115—116°.

With hydrogen chloride in an anhydrous solution, *o*-acetylaminobenzyl alcohol forms an *additive* compound, $\text{C}_9\text{H}_{12}\text{O}_2\text{NCl}$, which is obtained in glistening, delicate needles and melts at 120—125°. With alkalis, it does not regenerate *o*-acetylaminobenzyl alcohol, but yields 3-methyl-2:4-benzoxazine (μ -methylphenopentoxazole; Gabriel and Posner, *loc. cit.*). The *picrate* and the *platinichloride* of 3-methyl-2:4-benzoxazine can be obtained directly from the additive compound. The *platinichloride* is salmon-coloured and melts and decomposes at 219°. The *hydrochloride* is rapidly converted by water into the hydrochloride of *o*-aminobenzyl acetate.

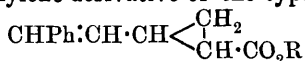
The action of hydrochloric acid on acetylaminobenzyl alcohol in presence of moisture or of hydrogen chloride on the dry acetate over sulphuric acid leads to the formation chiefly of the hydrochloride of *o*-aminobenzyl acetate. G. Y.

Reduction of Triphenylcarbinol. JOSEF HERZIG (*Ber.*, 1904, 37, 2107).—The reduction of triphenylcarbinol to triphenylmethane is described by Acree (this vol., i, 315), who omits to mention that this reduction had already been effected by Herzig and Wengraf (Abstr., 1901, i, 702). A. McK.

Lupeol. ERNST SCHULZE (*Zeit. physiol. Chem.*, 1904, 41, 474—476. Compare Likiernik, Abstr., 1891, 551 and 1446).—Lupeol from *Lupinus albus* appears to be identical with that from *L. luteus*.

Lupeol itself melts after several crystallisations at 211—212°, its benzoate at 265—266°, and its acetate at 141—142°. J. J. S.

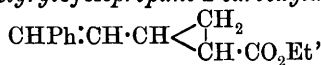
Ethyl Diazoacetate and Systems with Conjugated Double Linkings. CARL VON DER HEIDE (*Ber.*, 1904, 37, 2101—2106).—According to Thiele, in a conjugated system of contiguous double linkings, two univalent substituents take up the 1:4-position. To test how bivalent radicles behave in a similar case, the author has studied the action of ethyl diazoacetate on phenylbutadiene. The addition does not take place in the $\alpha\delta$ -position in the phenylbutadiene molecule, since a cyclopentene derivative is not produced. On the other hand, a trimethylene derivative of the type



is formed. The phenyl group thus prevents the formation of a tri-

methylene ring at the contiguous $\alpha\beta$ -double linking, so that the addition of the $(\text{CH}\cdot\text{CO}_2\text{R})<$ group at the end of the side-chain, accompanied by the closing of the ring, takes place with greater ease.

Phenylbutadiene was prepared by the action of magnesium methyl bromide on cinnamaldehyde (compare Klages, Abstr., 1902, i, 669); it was found convenient to decompose the crude product resulting from the Grignard reaction by sulphuric acid instead of by water, as directed by Klages. When phenylbutadiene (1 mol.) and ethyl diazoacetate (1 mol.) were heated for 30 hours at $70\text{--}90^\circ$, nitrogen was evolved and *ethyl 1-styrylcyclopropane-2-carboxylate*,



was formed; it melts at $42\text{--}43^\circ$ and decolorises alkaline permanganate.

1-Styrylcyclopropane-2-carboxylic acid, prepared by hydrolysis of the preceding ester, separates in colourless leaflets, of a mother-of-pearl lustre, or in prisms and melts at 130° . Its *amide* melts at 160° . Its *dibromide* forms glistening, white crystals and melts at $203\text{--}204^\circ$; it does not decolorise alkaline permanganate.

The constitution of *1-styrylcyclopropane-2-carboxylic acid* is proved by its yielding, on oxidation, a mixture of benzoic acid and *trans-cyclopropane-1;2-dicarboxylic acid*. When *1-styrylcyclopropane-2-carboxylic acid* was reduced by sodium in amyl alcohol solution, an acid was obtained, the amide of which melted at $95\text{--}96^\circ$; this acid is formed by the disruption of the trimethylene ring, and is either ϵ -phenylhexoic or δ -phenyl- β -methylvaleric acid. Conditions are quoted where normal reduction by sodium amalgam takes place without disruption of the trimethylene ring; the *amide* of *1- β -phenylethylcyclopropane-2-carboxylic acid* forms glistening leaflets and melts at $104\text{--}105^\circ$.
A. McK.

m-Aminobenzonitrile and some of its Derivatives. MARSTON T. BOGERT and HAL T. BEANS (*J. Amer. Chem. Soc.*, 1904, 26, 464—499. Compare Bogert and Hand, Abstr., 1903, i, 292).—*m-Aminobenzonitrile* may be prepared from *m*-nitroaniline by the Sandmeyer reaction or from benzonitrile by nitration and subsequent reduction of *m*-nitrobenzonitrile. *m-Nitrobenzonitrile* forms silky needles and melts at $117\text{--}117\cdot5^\circ$ (corr.). *m-Aminobenzonitrile* separates from ether in hexagonal prisms and from carbon tetrachloride in silky needles, which melt at $53\text{--}53\cdot5^\circ$ (corr.). Its *hydrochloride* crystallises from alcohol in pearly flakes. *iso*Phthalonitrile, $\text{C}_6\text{H}_4(\text{CN})_2$, separates from a mixture of ethyl acetate and light petroleum in needles and melts at $161\cdot5\text{--}162^\circ$ (corr.).

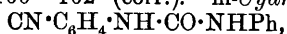
m-Formylaminobenzonitrile, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{COH}$, prepared from *m*-aminobenzonitrile and formic acid, separates from water in microscopic needles and melts at $150\cdot5\text{--}151^\circ$ (corr.). *m-Acetylaminobenzonitrile*, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$, obtained from *m*-aminobenzonitrile and acetic anhydride, separates from water in slender needles and melts at $130\cdot5\text{--}131^\circ$ (corr.). *m-Propionylaminobenzonitrile*, prepared from

m-aminobenzonitrile and propionic anhydride, separates from a mixture of benzene and light petroleum in needles and melts at 83.5—84° (corr.). *n*-Butyryl-*m*-aminobenzonitrile separates from a mixture of benzene and light petroleum and melts at 72.5—73.5° (corr.). isoButyryl-*m*-aminobenzonitrile separates from dilute alcohol in pearly flakes and melts at 101° (corr.). isoValeryl-*m*-aminobenzonitrile separates from a mixture of benzene and light petroleum in pearly flakes and melts at 77—78° (corr.). In those acyl compounds, accordingly, the melting point decreases with increase of carbon atoms in the aliphatic chain.

m-Acetylaminobenzamide, $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}_2$, prepared by hydrolysing *m*-acetylaminobenzonitrile with alkaline hydrogen peroxide, crystallises from water in fine needles and melts at 216—216.5° (corr.).

m-Benzoylaminobenzonitrile separates from dilute alcohol in pearly flakes and melts at 141.5—142° (corr.). 3-Nitrobenzoyl-*m*-aminobenzonitrile, best prepared by dissolving the *m*-aminobenzonitrile in pyridine and then adding a pyridine solution of *m*-nitrobenzoyl chloride, crystallises from alcohol in needles and melts at 196.5—197° (corr.). 4-Nitrobenzoyl-*m*-aminobenzonitrile separates from alcohol in yellow needles and melts at 250—251° (corr.). Benzenesulphonyl-*m*-aminobenzonitrile separates from aqueous alcohol in silky needles and melts at 126.5—127° (corr.).

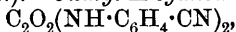
m-Cyanophenylurethane, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, prepared from *m*-aminobenzonitrile and ethyl chlorocarbonate, forms prismatic crystals and melts at 61—62° (corr.); when digested with hydrogen peroxide and sodium hydroxide, it forms *m*-urethanebenzamide, $\text{NH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, which crystallises in flakes and melts at 159—160°. *m*-Cyanophenylcarbamide, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, prepared from *m*-aminobenzonitrile hydrochloride and potassium cyanate, separates from a mixture of ethyl acetate and light petroleum in needles and melts at 160—162° (corr.). *m*-Cyanocarbaniide,



prepared from *m*-aminobenzonitrile and phenylcarbimide, crystallises from alcohol in needles and melts at 170.5—171° (corr.). When heated at 175°, it forms di-*m*-cyanocarbaniide, $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CN})_2$, which separates from alcohol in needles and melts at 199°. This may also be prepared from *m*-aminobenzonitrile and *m*-cyanophenylcarbamide or from *m*-aminobenzonitrile and carbonyl chloride. *m*-Cyanothiocabaniide, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$, prepared from *m*-aminobenzonitrile and phenylcarbimide, separates from chloroform in yellow, rhombic crystals and melts at 143—144° (corr.).

Ethyl *m*-cyano-oxanilate, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$, obtained from *m*-aminobenzonitrile and ethyl oxalate, crystallises from alcohol in needles and melts at 148—148.5° (corr.); when heated above its melting point, it decomposes into ethyl oxalate and oxaldi-*m*-cyanoanilide. *m*-Cyanophenylloxamide, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, prepared by the action of ammonia on ethyl *m*-cyano-oxanilate, separates from alcohol in pearly flakes and melts at 245—246° (corr.). Oxalyl-*m*-cyanoanilide, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{NHPh}$, prepared by heating ethyl *m*-cyano-

oxanilate with aniline, crystallises from alcohol in silky needles and melts at 205—206° (corr.). *Oxalyl-m-cyanoanilide*,



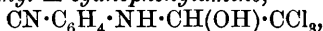
prepared by melting ethyl *m*-cyano-oxanilate (1 mol.) with *m*-aminobenzonitrile (1 mol.) in presence of anhydrous zinc chloride, crystallises from amyl alcohol and does not melt at 300°.

m-Cyanosuccinanilic acid, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, prepared from succinic anhydride and *m*-aminobenzonitrile, crystallises in silky flakes and melts at 132—133° (corr.); its *silver* and *calcium* salts were prepared, the latter crystallising with 4H₂O. Its *methyl ester* crystallises from dilute methyl alcohol in slender needles and melts at 88—89° (corr.). Its *ethyl ester* separates from a mixture of benzene and light petroleum in needles and melts at 84—84.5° (corr.). Its *amide*, prepared by the action of ammonia on its methyl or ethyl ester, crystallises from water in glistening plates and melts at 184° (corr.) if heated quickly. Its *acid chloride*, prepared by the action of phosphorus pentachloride, separates from chloroform in shining needles and

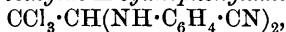
melts at 80° (corr.). *m*-Cyanosuccinanil, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{N} \begin{smallmatrix} \text{CO}\cdot\text{CH}_2 \\ \text{CO}\cdot\text{CH}_2 \end{smallmatrix}$, prepared by the action of acetic anhydride on *m*-cyanosuccinanilic acid, crystallises in needles and melts at 137—137.5° (corr.). By the action of alkaline hydrogen peroxide, it is converted into *m*-carbaminsuccinanilic acid, $\text{NH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which crystallises in needles and melts at 203—205° (corr.).

Condensation products of aromatic amines with chloral have been investigated by Wallach, Eibner, Wheeler, and others. Condensation products of *m*-aminobenzonitrile and chloral are described.

Trichlorohydroxyethyl-m-cyanophenylamine,



forms prismatic crystals and melts and decomposes at 102—103° (corr.) to form *trichloroethyl-di-m-cyanophenylamine*,

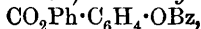


which is best prepared by the action of anhydrous chloral on *m*-aminobenzonitrile in toluene solution; it separates from aqueous alcohol in needles or in feathery plates and melts at 165—167° (corr.) when quickly heated. *Tribromoethyl-di-m-cyanophenylamine* chars to a black tar at about 130°.

Tribromo-m-aminobenzonitrile, prepared by brominating *m*-aminobenzonitrile in glacial acetic acid solution, crystallises from alcohol in needles and melts at 177—178°.

A. McK.

New Derivatives of Salol. ATTILIO PURGOTTI and N. MONTI (*Gazzetta*, 1904, 34, i, 267—278).—*Benzoylsalicylic acid*,



prepared by the action of benzoyl chloride on salol in presence of sodium hydroxide, crystallises from alcohol in shining needles, which melt at 80.5—81°, have no taste or smell, and dissolve slightly in the ordinary solvents. With ferric chloride, it gives the phenol reaction. On hydrolysis with alcoholic potassium hydroxide, it yields benzoic and

salicylic acids. Increasing doses, starting from 0.1 gram, of benzoyl salol were administered to two rabbits weighing 2.30 and 2.24 kilos. respectively, but the only effect produced, even with the largest doses, was a diminution in appetite.

Benzoylsalicylanilide, $\text{NHPh}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OBz}$, obtained together with phenol by the action of aniline (1 mol.) on benzoylsalol (1 mol.), separates from alcohol in colourless, acicular crystals melting at 180° .

Benzoylsalicyl-o-toluidide, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OBz}$, prepared from benzoylsalol and *o*-toluidine, is deposited from alcohol in shining crystals melting at 136° .

3-Bromo-5-nitrosalicylic acid,

$\text{CO}_2\text{Ph}\cdot\text{C}_6\text{H}_2\text{Br}(\text{NO}_2)\cdot\text{OH}$ [$\text{CO}_2\text{Ph} : \text{OH} : \text{Br} : \text{NO}_2 = 1 : 2 : 3 : 5$], prepared by the action of concentrated nitric acid (about 2 mols.) on an acetic acid solution of dibromosalol (1 mol.), separates from acetic acid in shining, colourless crystals melting at 165° .

3-Bromo-5-nitrosalicylanilide, $\text{NHPh}\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Br}(\text{NO}_2)\cdot\text{OH}$, prepared from the preceding compound and aniline, is deposited from alcohol in pale yellow crystals melting at 221° .

3-Bromo-5-nitrosalicyl-p-toluidide,

$\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Br}(\text{NO}_2)\cdot\text{OH}$, forms shining, golden-yellow needles, which blacken at 230° and melt at 256° .

3-Bromo-5-nitrosalicylphenylhydrazide,

$\text{NHPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Br}(\text{NO}_2)\cdot\text{OH}$, crystallises from alcohol in shining, yellow scales melting at 190° ; it reduces Fehling's solution in the cold and does not combine with aldehydes or ketones.

3-Bromo-5-nitrosalicylic acid also reacts readily with *o*-toluidine, yielding a *product* melting at about 250° . With α - and β -naphthylamines it reacts with difficulty, and with diphenylamine not at all.

T. H. P.

Bromo-derivatives of Indigotin. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 149899, 149940, and 149983. Compare Abstr., 1903, i, 345; this vol., i, 57, 167).—Pyridine dibromide, prepared by the addition of bromine to a solution of pyridine hydrochloride, reacts with indigotin at 90 – 100° , forming bromoindigotin and pyridine hydrobromide, the latter being recovered. Starch bromide also gives up its bromine to indigotin when intimately mixed with it, forming bromo- and dibromo-indigotin. The starch is converted into soluble starch and may be removed by boiling with water. Methyl-indigotin yields a blue monobromo- and a bluish-green dibromo-derivative.

Bromo-derivatives of indigotin may also be prepared by electrolysing solutions of bromides, in which indigotin or indigo-white is suspended. No diaphragm is necessary, as hydrogen has no action on the products. The method has the advantage that small quantities of bromine are always in presence of an excess of indigotin. The products closely resemble those obtained by dry bromination, but it has not yet been determined whether they are identical with them or with the products prepared synthetically from indoxyl.

C. H. D.

cycloGallipharic Acid. HERMANN KUNZ-KRAUZE and PAUL SCHELLE (*J. pr. Chem.*, 1904, [ii], 69, 385—386, 387—432. Compare Knoevenagel, *Abstr.*, 1896, i, 210).—After removal of gallic acid, ellagic acid, &c., from the residue of the ethereal extract obtained in the technical preparation of tannin from gall nuts there remains a green mass, from which *cyclogallipharic acid* is obtained by extraction with glacial acetic acid.

cycloGallipharic acid, $\text{OH} \cdot \text{C}_{20}\text{H}_{34} \cdot \text{CO}_2\text{H}$, crystallises from alcohol in sheaves of prisms, melts at 89° , and when heated above 200° evolves an aromatic, combustible gas, and acraldehyde when strongly heated, especially with potassium hydrogen sulphite. The acid is insoluble in water, but soluble in alcohol, ether, chloroform, benzene, carbon disulphide, light petroleum, aqueous alkalis, or ammonia. The silver salt,

$\text{C}_{20}\text{H}_{35}\text{O} \cdot \text{CO}_2\text{Ag}$,
and the calcium salt, $(\text{C}_{20}\text{H}_{35}\text{O} \cdot \text{CO}_2)_2\text{Ca}$, are described.

The acid dissolves in concentrated sulphuric acid with the formation of a colourless sulphonic acid which is soluble in water. On addition of sulphuric acid, the solution of *cyclogallipharic acid* in glacial acetic acid slowly assumes a green colour (Liebermann's cholesterol reaction), but in chloroform solution the addition of sulphuric acid produces no coloration.

The *acetyl* derivative, $\text{C}_{20}\text{H}_{34}(\text{CO}_2\text{H}) \cdot \text{OAc}$, crystallises in long, white prisms, melts at 71° , is soluble in aqueous alkalis, and gives no coloration with ferric chloride in neutral solutions. The *silver* salt,

$\text{C}_{20}\text{H}_{34}(\text{OAc}) \cdot \text{CO}_2\text{Ag}$,
is described.

Attempts to prepare a benzoyl derivative resulted, with the Schotten-Baumann method in a pasty mass, with Einhorn's method in an *additive* compound with pyridine, $\text{C}_{21}\text{H}_{36}\text{O}_3 \cdot \text{C}_5\text{H}_5\text{N}$.

The *ethyl* ester, $\text{C}_{20}\text{H}_{35}\text{O} \cdot \text{CO}_2\text{Et}$, crystallises in long, glistening needles and melts at 37° . With ferric chloride in alcoholic solution, it gives a violet coloration.

cycloGallipharic acid combines with 1 mol. of iodine; with bromine in aqueous solution it forms the compound $\text{C}_{21}\text{H}_{34}\text{O}_3\text{Br}_2 \cdot \text{HBr}$, which crystallises in small prisms, melts at 61° , and gives a violet coloration with ferric chloride. The ethyl ester forms the *bromine* compound, $\text{C}_{21}\text{H}_{35}\text{O}_3\text{Br}_2\text{Et}$, which melts at 46° .

The action of nitric acid on *cyclogallipharic acid* leads to the formation of oxalic acid, butyric acid, and two dinitro-compounds. The α -*dinitro*-compound, $\text{C}_{15}\text{H}_{24}\text{O}(\text{NO}_2)_2$, crystallises in colourless, prismatic needles, melting at 63.5° ; the β -*dinitro*-compound, $\text{C}_{15}\text{H}_{24}\text{O}(\text{NO}_2)_2$, crystallises in reddish-yellow leaflets and melts at 59.5° .

Reduction of the dinitro-compounds with zinc dust in aqueous solution, or with "excited" aluminium (Wislicenus, *Abstr.*, 1896, i, 671), leads to the formation of a *nitroamino*-compound, $\text{NO}_2 \cdot \text{C}_{15}\text{H}_{23}(\text{NH}_2) \cdot \text{OH}$, which crystallises with H_2O in green leaflets, melts at 47° , and is very unstable. When heated at 200° , *cyclogallipharic acid* loses carbon dioxide and yields a *ketoanhydride*, $\text{OH} \cdot \text{C}_{20}\text{H}_{34} \cdot \text{CO} \cdot \text{C}_{20}\text{H}_{34} \cdot \text{OH}$, which crystallises in fatty prisms, melts at 48° , is easily soluble to neutral solutions in organic solvents, and gives no coloration or precipitation with ferric chloride or silver nitrate.

When heated at 250° , *cyclogallipharic acid* yields *cyclogallipharol*, $C_{20}H_{35}\cdot OH$, or *cyclogallipharone*, $C_{19}H_{36}\cdot CO$, which crystallises in colourless needles, melts at 46° , and forms a *bromo-derivative*, crystallising in needles. It does not form a compound with hydroxylamine (compare Abstr., 1899, i, 200). The same derivative, $C_{20}H_{36}O$, is obtained along with hydrocarbons of the series C_nH_{2n} (heptene—undecene), when calcium *cyclogallipharate* is distilled; it is also formed along with acetic acid, oxalic acid, and 4-hydroxy-*m*-xylene when *cyclogallipharic acid* is fused with potassium hydroxide at 300° , or with aqueous potassium hydroxide at 150° under pressure. Oxidation of *cyclogallipharic acid* with potassium permanganate in alkaline solution leads to the formation of *n*-butyric acid, oxalic acid, glycerol, and gallipharic acid.

Gallipharic acid, $C_{15}H_{31}\cdot CO_2H$, crystallises in colourless needles, melts at 54° , and is insoluble in water, but soluble in organic solvents or dilute alkalis. It gives a yellow coloration with ferric chloride and a white, flocculent *precipitate* with silver nitrate. The acid does not form an additive compound with bromine.

On distillation with zinc dust, *cyclogallipharic acid* yields *m*-xylene and naphthalene.

cyclogallipharic acid is not reduced by sodium or sodium amalgam, but when heated with hydriodic acid and red phosphorus at 100° , yields a *substance* which is half melted at 15° , decolorises bromine water, and gives a white precipitate with ferric chloride. It is considered to be the hydrocarbon corresponding with *cyclogallipharic acid*.

G. Y.

Aromatic Butadienedicarboxylic Acids. I. HANS STOBBE (*Ber.*, 1904, 37, 2232—2236).—In acid solution, aldehydes react with succinic acid or its esters, yielding paraconic acids, which may be transformed into mono-substituted itaconic acids. In the presence of sodium ethoxide, aldehydes react with esters of succinic acid, yielding $\alpha\delta$ -disubstituted butadienedicarboxylic acids or γ -monosubstituted itaconic acids.

Condensations between ketones and esters of succinic acids do not occur in acid solution; in the presence of sodium ethoxide, the condensation is usually between equal number of molecules of the reacting substances, but in a very few cases two molecules of aldehyde react with one of the ester.

Aldehydes also readily condense with the esters of mono- and disubstituted itaconic acids, yielding di- and tri-substituted butadienedicarboxylic acids. As a rule, ketones do not react so readily, and the products are tri- and tetra-substituted butadienedicarboxylic acids.

The butadienedicarboxylic acids are sparingly soluble in water and the usual solvents. They are only faintly acid, and can be extracted from solutions of their salts by suitable solvents. Some are colourless, others yellow, and their melting points, as a rule, are above 200° ; at this temperature, the majority yield anhydrides. Permanganate oxidises them to oxalic acid and aldehydes or ketones, sodium amalgam reduces them to butanedicarboxylic acids, but towards alkalis they are relatively stable.

J. J. S.

Butadiene Derivatives. II. Coloured Anhydrides of Butadiene- $\beta\gamma$ -dicarboxylic Acids. HANS STOBBE (*Ber.*, 1904, 37, 2236—2240).—Butadiene- $\beta\gamma$ -dicarboxylic acids (compare preceding abstract) are readily transformed into anhydrides under the influence of acetyl chloride. These anhydrides are all coloured and often exhibit pleochroism; they are stable in the presence of water or sodium carbonate, but alkali hydroxides gradually hydrolyse them to the alkali salts of the acids. Dark-coloured intermediate products appear to be formed during the hydrolysis. The anhydrides dissolve in piperidine, yielding salts which are soluble in water and from which the free acids can readily be obtained. Under the action of light and heat, the anhydrides undergo changes in colour. This change is only temporary when the exposure is for a short time, but, on prolonged exposure, isomeric anhydrides are obtained.

The temporary change is a case of phototropy (compare Marckwald, *Abstr.*, 1900, ii, 2; Biltz, *ibid.*, ii, 125). The permanent change is most readily brought about in solution and yields isomerides, the constitutions of which have not been determined. J. J. S.

Butadiene Derivatives. III. Dibenzylidenesuccinic Acid. HANS STOBBE and PHOKION NAOÛM [and, in part, with KARL KAUTZSCH] (*Ber.*, 1904, 37, 2240—2249. Compare preceding abstracts).—Dibenzylidenesuccinic acid ($\alpha\delta$ -diphenylbutadiene- $\beta\gamma$ -dicarboxylic acid) (compare *Abstr.*, 1894, i, 595) may be obtained by the action of an ethereal solution of benzaldehyde on ethyl succinate in the presence of sodium ethoxide free from alcohol or from benzaldehyde and ethyl γ -phenylitaconate in an alcoholic solution of sodium ethoxide. Among the by-products obtained are benzyl alcohol, benzoic acid, phenylitaconic acid, phenylaticonic acid, and an unsaturated acid, $C_{17}H_{16}O_3$, melting at $170-171^\circ$, and its *ethyl* ester, which melts at $48-50^\circ$.

Dibenzylidenesuccinic acid crystallises from ether in glistening, four-sided plates containing a molecule of ether of crystallisation. The *sodium* salt contains $1H_2O$, which it loses at $140-160^\circ$. The *silver* salt is anhydrous, and the *barium* salt has the formula



The *piperidine* salt melts and decomposes at $181-182^\circ$ and is readily soluble in water. The *ethyl* ester crystallises in colourless prisms melting at 110.5° .

The *anhydride* obtained by the action of acetyl chloride on the acid forms large, yellow, triclinic crystals melting at $203-204^\circ$. It dissolves readily in chloroform and hot benzene and is not hydrolysed by hot water or sodium carbonate solution.

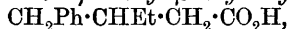
On oxidation, the acid yields oxalic and benzoic acids; acetic and malonic acids do not appear to be formed. Hot alkalis are practically without action on dibenzylidenesuccinic acid.

Both the acid and its ester, when exposed to sunlight in benzene solution and in presence of iodine, are transformed into isomerides.

J. J. S.

Condensation of Acetophenone with Ethyl Malonate. JOHAN F. EIJKMAN (*Chem. Centr.*, 1904, i, 1258—1259; from *Chem. Weekblad.*, 1, 349—372).—By the action of ethyl malonate on aceto-

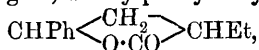
phenone in ethereal solution and in presence of sodium ethoxide, dypnone (compare Delacre and Gesché, Abstr., 1900, i, 603, 604), α -isodypnopinacolin, phenylmethylcarbinol (compare Stobbes, Abstr., 1901, i, 549), and β -ethylphenacylmalonic acid are formed. Dypnone and α -isodypnopinacolin are also formed by the action of sodium ethoxide on acetophenone. α -isodypnopinacolin separates from acetone in colourless crystals which melt at 134.5° ; it is sparingly soluble in cold ether or alcohol, but more so in the hot solvents. A saturated solution in 99.5 per cent. alcohol contains 0.425 per cent. By the action of bromine in glacial acetic acid or of phosphorus pentachloride it is converted into α -dehydroisodypnopinacolin, $C_{32}H_{24}O$, which crystallises from alcohol in colourless needles melting at 174.5° (compare Delacre, *Bull. Acad. roy. Belg.*, 1895, 855). β -Ethylphenacylmalonic acid, $COPh \cdot CHEt \cdot CH(CO_2H)_2$, crystallises from dilute alcohol in colourless crystals and melts and decomposes about 140° ; it is sparingly soluble in cold, but more soluble in boiling water or ether, and readily so in alcohol. The *ethyl ester* is a colourless liquid which has a sp. gr. 1.1012 at 22.1° and $n_D 1.49555$ at 22.1° . By the action of phenylhydrazine on a solution of the free acid in glacial acetic acid, a dibasic *hydrazonic acid*, $C_{19}H_{20}O_4N_2$, is formed, which crystallises from alcohol and melts and decomposes at 162° . If ether is used as a solvent instead of glacial acetic acid, the carboxyl groups are also attacked by the hydrazine and a *diphenylhydrazine* salt of the hydrazonic acid, $C_{31}H_{36}O_4N_6$, is formed. The latter compound is precipitated from its solution in alcohol by light petroleum in the form of a colourless, crystalline powder which melts with liberation of gas at 80° . β -Ethylphenacylacetic acid, $COPh \cdot CHEt \cdot CH_2 \cdot CO_2H$, crystallises from alcohol in colourless needles, melts at 78.5° , is soluble in ether or benzene, and has a sp. gr. 1.0878 at 79.05° and $n_D 1.50742$ at 79.05° . The *ethyl ester*, $C_{14}H_{18}O_3$, is a colourless liquid which boils at 175° under 20 mm. pressure, and has a sp. gr. 1.0612 at 17.9° and $n_D 1.50548$ at 17.9° . The *phenylhydrazone*, $C_{18}H_{20}O_2N_2$, separates from alcohol in colourless crystals and melts at 136° . When β -ethylphenacylacetic acid is warmed with excess of acetyl chloride, it appears to be converted into the enolic form, $OH \cdot CPh : CEt \cdot CH_2 \cdot CO_2H$, an amorphous acetate, $C_{14}H_{16}O_4$, being obtained, which has a sp. gr. 1.0843 at 78.9° and $n_D 1.51107$ at 78.9° ; it changes slowly into the original acid. *Dibromo- β -ethylphenacylacetic acid*, $C_{12}H_{12}O_3Br_2$, formed by the action of bromine on β -ethylphenacylacetic acid, crystallises from benzene and melts at 150° ; the whole of the bromine may be removed by the action of dilute alkalis. By the action of sodium amalgam, β -ethylphenacylacetic acid is reduced to β -ethylphenylbutyrolactone $CHEt \cdot \begin{matrix} \text{CHPh} \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CO} \end{matrix} \cdot O$, which crystallises from alcohol in colourless needles melting at 88° ; it boils at 165° under 3 mm. pressure, has a sp. gr. 1.0525 at 86.1° and $n_D 1.50715$ at 86.1° , and is very sparingly soluble in light petroleum. γ -Phenyl- β -ethylbutyric acid,



prepared by heating the lactone with hydriodic acid of sp. gr. 1.7 at 170 – 180° , crystallises from alcohol, melts at 22° , boils at 134° under 1 mm. pressure, and has a sp. gr. 1.0339 at 13.4° and $n_D 1.50862$

at 13.4° ; the calcium salt, $\text{Ca}(\text{C}_{12}\text{H}_{15}\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$, is sparingly soluble in water and melts at the temperature of the water-bath. By the dry distillation of β -ethylphenacylacetic acid or β -ethylphenacylmalonic acid with lime, acetophenone is formed, and both these acids on oxidation with potassium permanganate give a nearly quantitative yield of benzoic acid. α -Ethylphenacylmalonic acid, $\text{COPh} \cdot \text{CH}_2 \cdot \text{CEt}(\text{CO}_2\text{H})_2$ (compare Dittrich and Paal, Abstr., 1889, i, 257), crystallises from chloroform forming a compound of the composition $2\text{C}_{13}\text{H}_{14}\text{O}_5 \cdot \text{CHCl}_3$. Diphenacylmalonic acid, $\text{C}(\text{CH}_2 \cdot \text{COPh})_2(\text{CO}_2\text{H})_2$ (compare Kuess and Paal, Abstr., 1887, 261), also forms a crystalline compound with 1 mol. of chloroform. By the action of phenylhydrazine (1 mol.) on α -ethylphenacylmalonic acid, 2 mols. of water are eliminated and an acid is formed which melts at 134° and probably has the composition $\text{N} \begin{smallmatrix} \diagup \text{NPh} - \text{CO} \\ \diagdown \text{CPh} \cdot \text{CH}_2 \end{smallmatrix} \text{CEt} \cdot \text{CO}_2\text{H}$.

When an ethereal solution of the acid is used, however, *diphenylhydrazine α -ethylphenacylmalonate*, $\text{C}_{25}\text{H}_{30}\text{O}_5\text{N}_4$, is obtained in the form of a white, crystalline precipitate which melts and liberates gas at 113° . When α -ethylphenacylacetic acid, which is prepared by heating the corresponding malonic acid above its melting point, is reduced by sodium amalgam, α -ethylphenylbutyrolactone,



is formed; it crystallises from ether, melts at 30° , and has a sp. gr. 1.0920 at 13.5° and n_D 1.52435 at 13.5° .

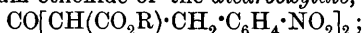
Phenylbutyrolactone and ethyl benzoylpropionate have been prepared from benzoylpropionic acid by the usual methods; the former melts at 37° and boils at 128° under 2 mm. pressure, whilst the latter boils at 128° under 2 mm. and at 184° under 22 mm. pressure. The following data have also been experimentally determined, the sp. gr. and n_D being measured in each case at the same temperature:

| | Sp. gr. | n_D . | Temp. |
|------------------------------|---------|---------|----------------|
| Phenylbutyrolactone | 1.1554 | 1.54184 | 15.4° |
| | 1.1042 | 1.51591 | 80.15 |
| Ethyl benzoylpropionate ... | 1.1068 | 1.51408 | 13.5 |
| Acetophenone..... | 1.0297 | 1.53017 | 17.6 |
| | 0.9781 | 1.50160 | 77.6 |
| Phenyl ethyl ketone | 1.0133 | 1.52461 | 15.7 |
| Phenyl undecyl ketone | 0.87935 | 1.47001 | 78.5 |
| Phenyl pentadecyl ketone... | 0.8692 | 1.46746 | 75.9 |

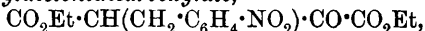
The values of the molecular refraction and molecular dispersion calculated from the so-called atomic constants do not agree with the results of actual measurement,
E. W. W.

Nitrobenzylated Ethyl Acetonedicarboxylates. FRITZ FICHTER and CHASKEL WORTSMANN (*Ber.*, 1904, 37, 1992—1997).—On adding an alcoholic solution of ethyl sodioacetonedicarboxylate to a hot alcoholic solution of *p*-nitrobenzyl chloride (1 mol.), *ethyl as-di-p-nitrobenzylacetonedicarboxylate*, $\text{CO}_2\text{Et} \cdot \text{C}(\text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2)_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, is obtained; it separates from glacial acetic acid in large, lustrous

crystals, melts at 118—119°, and is hydrolysed by boiling hydrochloric acid to *as-di-p-nitrobenzylacetone*, $\text{CH}(\text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2)_2 \cdot \text{CO} \cdot \text{CH}_3$, which crystallises from alcohol in thin, flexible, silky needles melting at 108.5—109.5°. Simultaneously with the asymmetrical dicarboxylate is produced *s-di-p-nitrobenzylacetone*, $\text{CO}(\text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$, which crystallises from alcohol or glacial acetic acid in slender, lustrous needles, melts at 136—138°, and is probably formed owing to the hydrolysis by sodium ethoxide of the *dicarboxylate*,

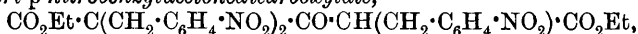


the latter substance, however, could not be isolated. The presence of *ethyl p-nitrobenzylacetonedicarboxylate*,

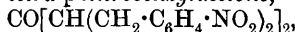


in the oily mother liquors is proved by their giving *p-nitrobenzylacetone*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2\text{Ac}$, on hydrolysis with hydrochloric acid; this ketone is isolated by means of its sodium hydrogen sulphite derivative and melts at 40—41°. The acid products of this hydrolysis are *p-nitrohydrocinnamic acid*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, and *di-p-nitrobenzoylacetic acid*.

By acting with 2 mols. of *p-nitrobenzyl chloride* on *ethyl sodioacetonedicarboxylate*, the same products are obtained as with 1 mol., but using the proportion required for a tri-*p-nitrobenzyl derivative*, *ethyl tri-p-nitrobenzylacetonedicarboxylate*,



is obtained. It crystallises from glacial acetic acid in lustrous, slightly yellow needles, melts at 167.5—168.5°, and is hydrolysed by hydrochloric acid to form *p-nitrohydrocinnamic acid* and *di-p-nitrobenzylacetic acid*. Together with the tri-*p-nitrobenzyl derivative* there is formed *tetra-p-nitrobenzylacetone*,



which separates from nitrobenzene on adding alcohol in colourless crystals and melts at 194—195°; it is produced by the hydrolysis of a corresponding dicarboxylate. Some *ethyl di-p-nitrobenzylacetate*, $\text{CO}_2\text{Et} \cdot \text{CH}(\text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$, crystallising from alcohol or glacial acetic acid in white needles and melting at 104.5°, was also isolated and was identified by hydrolysing it to the corresponding acid.

W. A. D.

Synthesis of Benzene Derivatives from Ethyl Glutaconate.
HANS VON PECHMANN, WILHELM BAUER, and JULIUS OBERMILLER (*Ber.*, 1904, 37, 2113—2122).—*Ethyl 5-hydroxy-2:4-dicarboxydihydrocyclohexadieneacetate*, $\text{OH} \cdot \text{C}_6\text{H}_4(\text{CO}_2\text{Et})_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, produced on condensing ethyl glutaconate with sodium ethoxide, crystallises in colourless needles melting at 82° and gives a deep blue coloration with ferric chloride. The *diethyl ester*, formed by cautiously hydrolysing the triethyl ester with alcoholic potash, crystallises in colourless needles, melts without decomposition at 112—113°, gives a blue coloration with iron chloride, and is very soluble in alkali hydroxides. The *monoethyl ester*, produced from either of these esters by heating with 10 per cent. potassium hydroxide, crystallises in platelets melting and decomposing at 154°.

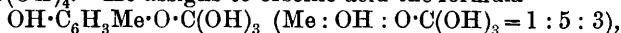
Ethyl 5-hydroxy-2:4-dicarboxyphenylacetate, obtained by oxidising

the foregoing triethyl ester with bromine, crystallises in colourless needles melting at 81° , gives a cherry-red coloration with ferric chloride, and does not decolorise permanganate; the *acetyl* derivative melts at 59° and does not give a coloration with ferric chloride. The *methyl* ether forms colourless, silky needles melting at 87° .

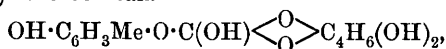
5-Hydroxy-2:4-dicarboxyphenylacetic acid, prepared by boiling the triethyl ester with potassium hydroxide, crystallises in colourless needles melting at $250-255^{\circ}$; the *acid potassium* salt melts at 212° . When heated with hydrogen chloride at 200° , it forms *m*-hydroxyphenylacetic acid. Tribromo-*m*-hydroxyphenylacetic acid is formed either by directly brominating the acid or on saturating the aqueous solution of the dicarboxylic acid with hydrogen bromide; it crystallises in long, colourless needles melting at 237° .

By the condensation of ethyl glutaconate and sodium ethoxide, 4-hydroxyethyl isophthalate is also formed; this melts at 57° and on hydrolysis gives the 4-hydroxyisophthalic acid described by Lawrence and Perkin (*Proc.*, 1901, 17, 47). E. F. A.

Erythrin (Erythric Acid). PAUL JUILLARD (*Bull. Soc. chim.*, 1904, [iii], 31, 610—615).—Erythrin, obtained by the extraction of orchil lichens with neutral solvents, has the formula $C_{40}H_{44}O_{20} \cdot 2H_2O$, is crystalline, melts at $146-148^{\circ}$, and is slightly soluble in the ordinary solvents. When treated with lime, it absorbs a molecule of water forming anhydroerythric acid, $C_{40}H_{46}O_{21}$, which, when dissolved in alcohol, decomposes into "simple erythrin," $C_{20}H_{22}O_{10} \cdot H_2O$, which melts at 138° and is the principal constituent of the "erythric acid" obtained by Stenhouse, Hesse, and others by the extraction of lichens with alkaline liquids. These three substances, when dissolved in hot alcohol, furnish picroerythrin and ethyl orsellate. The author proposes to represent these substances as derivatives of orthocarbonic acid, $C(OH)_4$. He assigns to orsellic acid the formula

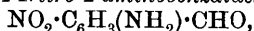


and represents the combination of erythritol with this to form picroerythrin by the formula



whilst to anhydroerythric acid, erythric acid, and the related substances β -picroerythrin, β -orsellic and lecanoric acids, formulæ derived from these are assigned. T. A. H.

p-Substituted *o*-Nitrobenzaldehydes. FRANZ SACHS and EMIL SICHEL (*Ber.*, 1904, 37, 1861—1874. Compare *Abstr.*, 1902, i, 377, 682; this vol., i, 62).—4-Nitro-2-aminobenzaldehyde,

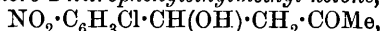


prepared by reducing 2:4-dinitrobenzaldehyde by titanium trichloride (Knecht, *Abstr.*, 1903, ii, 217), crystallises from water in slender needles and melts at 124° . Its *phenylbenzylhydrazone* separates from aqueous alcohol in glistening, violet plates and melts at 155° . Its *semicarbazone* forms reddish-yellow crystals, decomposes at about 390° . Its *oxime* separates from a mixture of acetone and water in bright

yellow crystals and melts at 193°. Its *anil* separates from dilute alcohol in red crystals and melts at 147°.

4-Chloro-2-nitrobenzaldoxime, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{CH} \cdot \text{NOH}$, prepared from 4-chloro-2-nitrobenzaldehyde, separates from ethyl alcohol in glistening threads and melts at 172°. 1-Phenyl-4-p-chloro-o-nitrobenzylidene-3-methylpyrazolone, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{CH} \cdot \text{C} \begin{smallmatrix} \text{CO}-\text{NPh} \\ \text{CMe} \cdot \text{N} \end{smallmatrix}$, forms dark red crystals and melts at 180°.

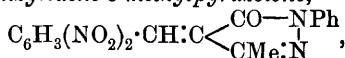
4-Chloro-2-nitrobenzylideneaniline, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{CH} \cdot \text{NPh}$, separates from ethyl alcohol in yellowish-white needles and melts at 93°. β -Hydroxy- β -4-chloro-2-nitrophenylethylmethyl ketone,



prepared by condensation of 4-chloro-2-nitrobenzaldehyde with acetone in presence of trisodium phosphate, crystallises from water in fan-shaped rods and melts at 76°. When its solution is warmed and a few drops of sodium hydroxide or sodium carbonate solution added (compare this vol., i, 325), dichloroindigotin is precipitated as a reddish-violet, flocculent precipitate. 4-Chloro-2-nitrostyryl methyl ketone, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{CH} \cdot \text{CH} \cdot \text{COMe}$, prepared by warming β -hydroxy- β -4-chloro-2-nitrophenylethyl methyl ketone with acetic anhydride and sodium acetate, crystallises from dilute alcohol in stellate rods and melts at 102°.

4-Bromo-2-nitrobenzaldehyde, prepared by heating 2-nitro-4-aminobenzaldehyde with ferric sulphate and hydrobromic acid, is identical with the compound previously prepared by Sachs and Kempf by the application of the Sandmeyer reaction to 2-nitro-4-aminobenzaldehyde. Its *semicarbazone* separates from glacial acetic acid in yellowish-white crystals and melts at 276°. Its *oxime* crystallises from aqueous ethyl alcohol in white scales and melts at 164°. β -Hydroxy- β -4-bromo-2-nitrophenylethyl methyl ketone, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{COMe}$, melts at 92° and yields dibromoindigotin by the action of sodium hydroxide or sodium carbonate. 4-Bromo-2-nitrostyryl methyl ketone crystallises from dilute alcohol in snow-white needles and melts at 109°. 4-Bromo-2-nitrobenzylideneaniline separates from dilute alcohol in silky needles and melts at 105°.

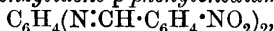
2:4-Dinitrobenzaldehyde acetal, $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{CH}(\text{OMe})_2$, prepared by the action of a solution of hydrogen chloride in methyl alcohol on 2:4-dinitrobenzaldehyde, boils at 183–185° under 13 mm. pressure. 1-Phenyl-4-dinitrobenzylidene-3-methylpyrazolone,



melts at 160°.

1-Phenyl-4-o-nitrobenzylidene-3-methylpyrazolone melts at 154°.

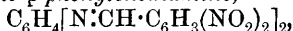
When a solution of *p*-chloro-o-nitrobenzylideneaniline in toluene is exposed to direct sunlight for four weeks, snow-white crystals of 4-chloro-2-nitrosobenzanilide, $\text{NO} \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{CO} \cdot \text{NPh}$, melting at 170°, separate. Bis-o-nitrobenzylidene-*p*-phenylenediamine,



prepared from *o*-nitrobenzaldehyde, *p*-phenylenediamine hydrochloride, and sodium acetate, separates from acetone in needles and melts at

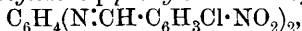
208° When first prepared, it is bright yellow; it gradually becomes, in the course of a dull winter's day, golden-bronze and then greyish-green, and after two days greyish-black.

Bisdinitrobenzylidene-p-phenylenediamine,



separates from toluene in golden-yellow needles and melts at 252°.

Bis-p-chloro-o-nitrobenzylidene-p-phenylenediamine,



melts at 230°. It is at first bright yellow; this colour gradually changes through golden-bronze and green to brownish-black under the influence of light.

4-Bromo-2-nitrosobenzoic acid, prepared by exposing a solution of *p*-bromo-*o*-nitrobenzaldehyde in a mixture of benzene and toluene to the action of light of 2½ weeks, separates in snow-white, rhombic plates, which melt at 222—225°. *Ethyl 4-bromo-2-nitrosobenzoate*, $\text{NO}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CO}_2\text{Et}$, prepared by the action of light on an alcoholic solution of *o*-nitro-*p*-bromobenzaldehyde, separates from alcohol in rhombic prisms and melts at 155°. It condenses with *p*-nitrobenzylcyanide to form the 2-carbethoxy-5-bromoanil of *p*-nitrobenzoylcyanide, $\text{NO}_2\cdot\text{C}_6\text{H}_4(\text{CN})\cdot\text{C}:\text{N}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CO}_2\text{Et}$, which melts at 144°.

4-Chloro-2-aminobenzaldehyde, prepared by reducing 4-chloro-2-nitrobenzaldehyde with titanium chloride, crystallises from alcohol in long needles and melts at 86°. Its *phenylhydrazone* separates from dilute ethyl alcohol in white leaflets, with a mother-of-pearl lustre, and melts at 230°. *1-Phenyl-4-p-chloro-o-aminobenzylidene-3-methylpyrazolone* derivative melts at 265°.

A. MCK.

Preparation of Four Isomeric Methylionones. HAARMANN and REIMER (D.R.-P. 150827).—In the preparation of alkylated ψ -ionones, the aldehyde group of the citral may react either with the methyl group of the ketone, or with the adjoining methylene group, and each of the isomerides thus produced may occur in two forms, corresponding with α - and β -ionones. Both α - and β -methylionones (Abstr., 1902, 1, 471) contain two isomerides, one of which (the α -form) dissolves readily in sodium hydrogen sulphite, the β -form being sparingly soluble. ψ -Methylionone may in a similar manner be separated into a readily and a more sparingly soluble constituent, which may then be converted into the corresponding methylionones.

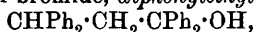
a- α -Methylionone boils at 137—142° (uncorr.) under 15 mm. pressure and has a sp. gr. 0.927 and n_D 1.5009 at 20°; its *semicarbazone* melts at 144°. *b*- α -Methylionone boils at 135—140° under 15 mm. pressure, and has a sp. gr. 0.931 and n_D 1.5003 at 20°; the *semicarbazone* melts at 202°.

a- β -Methylionone boils at 145—151° under 15 mm. pressure, and has a sp. gr. 0.935 and n_D 1.5097 at 20°; its *semicarbazone* melts at 138—139°. *b*- β -Methylionone boils at 135—140° under 15 mm. pressure, and has a sp. gr. 0.936 and n_D 1.5073 at 20°; the *semicarbazone* melts at 175—176°.

C. H. D.

Reaction between Unsaturated Compounds and Organic Magnesium Compounds. ELMER P. KOHLER (*Amer. Chem. J.*, 1904, 31, 642—661).—A further study of the substance obtained by the

interaction of benzylideneacetophenone and magnesium phenyl bromide (Abstr., 1903, i, 483) has shown that this product is not diphenylstyrylcarbinol, but consists of the isomeric ketone, *diphenylpropio-phenone*, $\text{CHPh}_2 \cdot \text{CH}_2 \cdot \text{COPh}$, which can also be prepared by the condensation of benzylideneacetophenone with benzene in presence of concentrated sulphuric acid. Its *phenylhydrazone* crystallises in pale yellow needles and melts at 137° ; the *oxime* melts at 131° , and by the action of phosphorus pentachloride is converted into *diphenylpropion-anilide*, which melts at 167° . When diphenylpropio-phenone is treated with magnesium phenyl bromide, *diphenylethylidiphenylcarbinol*,



is produced, which crystallises in needles, melts at $95-96^\circ$, and is readily soluble in alcohol or ether; the same substance is formed by the action of magnesium phenyl bromide on methyl diphenylpropionate. *Bromodiphenylpropio-phenone*, $\text{CHPh}_2 \cdot \text{CHBr} \cdot \text{COPh}$, prepared by the action of bromine on the magnesium compound formed in the reaction between benzylideneacetophenone and magnesium phenyl bromide, crystallises in colourless needles and melts at 173° . *Benzoyltriphenylpropenol*, $\text{CHPh}_2 \cdot \text{CH} \cdot \text{CPh} \cdot \text{OBz}$, obtained by the action of benzoyl chloride on the magnesium compound, crystallises in long, transparent needles, melts at 220° , and is soluble in hot chloroform or hot benzene; when warmed with a strong solution of potassium hydroxide containing a little alcohol, it is decomposed with formation of diphenylpropio-phenone and potassium benzoate.

When benzylideneacetophenone is treated with magnesium methyl iodide, phenylbutyrophenone is produced, which melts at 74° and yields an *oxime* melting at 93° .

Diphenylisobutyrophenone, $\text{CHPh}_2 \cdot \text{CHMe} \cdot \text{COPh}$, obtained by the interaction of benzylidenepropio-phenone and magnesium phenyl bromide, crystallises in needles or plates, melts at 105° , and is readily soluble in alcohol or ether and moderately so in light petroleum; the *oxime* melts at 145° .

$\beta\beta$ -*Diphenylbutyrophenone*, $\text{CPh}_2\text{Me} \cdot \text{CH}_2 \cdot \text{COPh}$, prepared by the action of magnesium phenyl bromide on dypnone, crystallises in thick prisms, melts at 103° , and dissolves readily in alcohol, acetone, or ether; the *oxime* melts at 163° .

When the product of the interaction of magnesium phenyl bromide and benzylideneacetone is decomposed with ice and hydrochloric acid, the tertiary *alcohol*, $\text{CHPh} \cdot \text{CH} \cdot \text{CPhMe} \cdot \text{OH}$, is produced as an oil which, on oxidation with cold neutral solution of potassium permanganate, yields benzoic and α -phenyl-lactic acids.

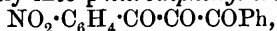
By the action of magnesium phenyl bromide on cinnamaldehyde, an oily product, probably the secondary *alcohol*, $\text{CHPh} \cdot \text{CH} \cdot \text{CHPh} \cdot \text{OH}$, is obtained, which, on oxidation, is converted into benzylideneacetophenone. Magnesium phenyl bromide reacts in a similar manner with α -bromo-cinnamaldehyde.

E. G.

Action of Nitrous Gases on 1:3-Diketones. HEINRICH WIELAND and SIEGFRIED BLOCH (*Ber.*, 1904, 37, 1524-1536).—*Bis-nitrosodibenzoylmethane*, $\text{CHBz}_2 \cdot \text{N}_2\text{O}_2 \cdot \text{CHBz}_2$, obtained on passing the nitrous fumes evolved from arsenious oxide and nitric acid into an

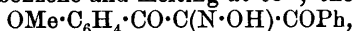
absolute ethereal solution of dibenzoylmethane, forms a white powder which is insoluble in most solvents and melts and decomposes at 125° ; it is decomposed by boiling alcohol or more easily by cold alcoholic potassium hydroxide or ammonia, giving the oxime $\text{CBz}_2\text{N}\cdot\text{OH}$ (von Pechmann, Abstr., 1891, 318). This oxime is rapidly hydrolysed by 20 per cent. sodium hydroxide forming benzoic acid and hydrogen cyanide. From the ethereal mother liquors of bisnitrosodibenzoylmethane, diphenyl triketone, $\text{COPh}\cdot\text{CO}\cdot\text{COPh}$ (von Pechmann, *loc. cit.*), separates as the crystalline hydrate. In order to convert the whole of the dibenzoylmethane into the triketone, the bisnitroso-derivative is converted by cold dilute alcoholic potassium hydroxide into the foregoing oxime, and this is then decomposed in ethereal solution by the nitrous gases.

When *p*-nitrodibenzoylmethane is exposed in benzene solution to the action of the nitrous fumes, it does not give a bisnitroso-derivative, but is converted directly into *p*-nitrodiphenyl triketone,



which crystallises from benzene or carbon disulphide and melts at 98 — 99° ; it readily absorbs water in alcoholic glacial acetic acid solution to form the *hydrate*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}(\text{OH})_2\cdot\text{COPh}$, which melts indefinitely at about 100° . By boiling water, the triketone is hydrolysed to *p*-nitrobenzoic acid, and with phenylhydrazine, it gives the *diphenylhydrazone*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{N}_2\text{HPh})\cdot\text{CO}\cdot\text{C}(\text{N}_2\text{HPh})\cdot\text{C}_6\text{H}_5$, which crystallises from glacial acetic acid in vermilion-coloured needles and melts at 219° .

Bisnitrosobenzoyl-p-anisoylmethane, $(\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CHBz})_2\text{N}_2\text{O}_2$, prepared from anisoylbenzoylmethane in absolute ethereal solution, melts and decomposes at 115 — 116° ; from the mother liquors of this substance, *phenylanisyltriketone*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CO}\cdot\text{COPh}$, is obtained, crystallising from benzene and melting at 65° ; the *oxime*,



forms colourless leaflets and melt at 127° .

Bisnitrosobenzoylacetone, $\text{N}_2\text{O}_2(\text{CHAcBz})_2$, prepared from benzoylacetone, melts and decomposes at 65° ; by alcohol at 30° , it is transformed into the oxime, $\text{COPh}\cdot\text{CAc}\cdot\text{N}\cdot\text{OH}$, but the product is only purified with difficulty.

W. A. D.

Quinonesulphonic Acid. GUSTAV SCHULTZ and R. STABLE (*J. pr. Chem.*, 1904, [ii], 69, 334—346).—4-Aminophenol-3-sulphonic acid is obtained by acting on *m*-phenolsulphonic acid with diazobenzene chloride in presence of sodium hydroxide and reducing the resulting *azo*-compound with stannous chloride and hydrochloric acid. It crystallises in sheaves of delicate, glistening needles, commences to blacken at 270° , decomposes at 285° , and is more soluble in water than 4-aminophenol-2-sulphonic acid or 2-aminophenol-4-sulphonic acid. It reduces ammoniacal silver solutions, gives a brownish-violet coloration with neutral ferric chloride, yields quinone on energetic oxidation, and forms bromanil when heated with an excess of bromine. The *potassium* and *barium* salts are described. The action of nitrous acid on 4-aminophenol-3-sulphonic acid leads to the formation of 4-diazophenol-3-sulphonic acid, $\text{OH}\cdot\text{N}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{SO}_3\text{H}$, which crys-

tallises in small, colourless tetrahedra or prisms, loses H_2O at 110° , and melts and decomposes at 189° . It is only slightly soluble in water, gives dyes with β -naphthol and sodium β -naphtholdisulphonate in alkaline solution, is reduced to aminohydroxybenzenesulphonic acid by stannous chloride and hydrochloric acid, and when heated at 180° with sulphuric acid yields quinol. Diazophenolsulphonic acid is also formed by the action of nitrous acid on 4-aminophenol-3-sulphonic acid (compare Bennewitz, *J. pr. Chem.*, 1873, [ii], 8, 52).

Quinonesulphonic acid is formed on oxidation of quinolsulphonic acid (Seyda, Abstr., 1883, 1115) by lead peroxide and sulphuric acid. A small amount of the free acid (?) is obtained in yellow, transparent prisms on addition of alcohol and ether. On addition of potassium chloride to the oxidation product, the *potassium* salt, $C_6H_3O_2 \cdot SO_3K$, is precipitated. Quinonesulphonic acid is also formed to a small extent by oxidation of 4-aminophenol-3-sulphonic acid, but a good yield is obtained by oxidation of the isomeride $[OH : SO_3H : NH_2 = 1 : 2 : 4]$ with sulphuric acid and lead peroxide, when part of the product separates as the *ammonium* salt, $C_6H_3O_2 \cdot SO_3NH_4$, and the remainder is precipitated by addition of potassium chloride. The potassium salt crystallises in scarlet prisms and decomposes at 235° ; the ammonium salt forms golden, microscopic plates and decomposes at 190 — 195° . These salts give a greenish-black coloration with ferric chloride in aqueous solution, reduce ammoniacal silver solutions, and form quinhydrone with quinol in aqueous solution. The potassium salt is reduced by sulphur dioxide, with formation of potassium quinolsulphonate. With amines, the potassium and ammonium salts form anilino-compounds: with aniline, a brown, flocculent *precipitate*, soluble in concentrated sulphuric acid to a violet solution; with *p*-toluidine, a brown *precipitate* which dissolves in sulphuric acid to a dark blue solution; with diphenylamine, a bluish-green *precipitate*, soluble in sulphuric acid with a blue colour; with *m*-phenylenediamine, an intense red coloration in aqueous solution. G. Y.

Uses of Naphthaquinonesulphonic Acid. PAUL EHRLICH and C. A. HERTER (*Zeit. physiol. Chem.*, 1904, 41, 379—392. Compare Witt, Abstr., 1892, 196; Bönninger, *ibid.*, 1894, i, 199).—Witt's 1:2-naphthaquinone-4-sulphonic acid in the form of its sodium derivative readily reacts with aromatic amines yielding compounds of the type of anilidonaphthaquinone, $C_6H_4 \begin{matrix} \text{CO} & \text{---} & \text{C} \cdot \text{OH} \\ & \diagdown & | \\ & \text{C}(\text{NPh}) & \text{CH} \end{matrix}$, in the form of red precipitates. The reaction is extremely delicate, and is given by most aromatic amines except when several strongly negative groups are present in the benzene ring. Aminocarboxylic acids, amino-sulphonic acids, diamines and amines derived from naphthalene give similar reactions.

The sulphonic acid also yields characteristic colorations in the presence of sodium carbonate with methylene derivatives of the type of ethyl acetoacetate, deoxybenzoin, and cyanoacetamide. Further, resorcinol, phloroglucinol, aliphatic primary amines, secondary amines, pectones, tyrosine, uric acid, &c., give colorations with the acid.

The sulphonic acid is extremely useful for locating aniline or other compounds which have been injected into the animal system. The dyes obtained by condensing the quinone mono- or di-sulphonic acid with dimethyl-*p*-phenylenediaminethiosulphonic acid are extremely useful for staining different tissues. The organs are not coloured when both reacting substances are injected or when the sulphonic acid is injected and the section treated with an amine. This is probably due to the reduction of the quinonesulphonic acid to a quinol derivative in the animal system.

1 : 2-Naphthaquinone-4 : 6-disulphonic acid reacts in much the same manner as the mono-sulphonic acid, and the condensation products are soluble in alkalis.

J. J. S.

Preparation of Dyes of the Anthracene Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 151018).—The sulphonic acids of aromatic amines condense with halogenated hydroxyanthraquinones to form dyes. Thus bromopurpurin, prepared by brominating purpurin in boiling acetic acid, chloropurpurin, prepared by chlorinating purpurin suspended in hydrochloric acid, or chloroalizarin may be heated with sodium sulphanilate at 200° under pressure, forming bronze-coloured crystals.

C. H. D.

Reduction of Cineole. HERMANN THOMS and B. MOLLE (*Arch. Pharm.*, 1904, 242, 181—194).—Attempts to reduce cineol, $C_{10}H_{18}O$, with various reducing agents only gave a satisfactory result when the substance was heated with hydriodic acid of sp. gr. 1.96 in the presence of a slight excess of metallic mercury, the sealed tubes containing the mixture being heated gradually to 220—225°, maintained for an hour at that temperature, and then allowed to cool gradually. In these circumstances, only 20 per cent. of the tubes burst. The gas formed consisted chiefly of hydrogen, but contained a little carbon dioxide and hydrogen iodide. The liquid product of the reaction was distilled with steam, and the oil which distilled was freed from mercuric iodide by allowing it to remain with a spiral of reduced copper, and then fractionated. Its chief constituent was a hydrocarbon, $C_{10}H_{18}$, named *cinolene*; this boils at 165—167° under 753 mm. pressure and has sp. gr. 0.8240 at 18°, 0.8227 at 20.5°; n_D 1.45993; and is optically inactive. When treated with bromine in chloroform solution, it does not merely form an additive compound, but evolves hydrogen bromide. When it is allowed to remain with hydrogen iodide in acetic acid solution at 0° and the solution then heated with silver acetate, an *acetate*, $C_{10}H_{19} \cdot OAc$, seems to be formed to some extent; and this, when hydrolysed with alcoholic potassium hydroxide, seems to yield an *alcohol*, $C_{10}H_{19} \cdot OH$. Concentrated sulphuric acid converts the hydrocarbon into α : 2-cymenesulphonic acid. It was not found possible to prepare a hydrochloride, nitrosochloride, nitrosite, or nitrosate; neither could a definite product be obtained by oxidation. Probably the hydrocarbon has the constitution $CHMe_2 \cdot CH < \begin{smallmatrix} CH=CH \\ CH_2 \cdot CH_2 \end{smallmatrix} > CHMe_2$.

Accompanying this product of the reduction of cineole is another

hydrocarbon ($C_{10}H_{16}$)_x, which boils at 200—245° under 22 mm. pressure and resembles vaselin in appearance. C. F. B.

A New Method of preparing Alkyl and Alkylidene Derivatives of Cyclic Ketones. Alkyl Derivatives of Menthone. ALBIN HALLER (*Compt. rend.*, 1904, 1139—1142).—Sodamide reacts

with cyclic ketones according to the equation $R-\text{C}(\text{CH}_3)_2-\text{CO} + \text{NaNH}_2 = R-\text{C}(\text{CH}_3)_2-\text{CO}^-\text{Na} + \text{NH}_3$. The product is free from the sodium derivative of

the corresponding alcohol and is therefore suitable for preparing pure alkyl derivatives of the ketone. The alkylmenthones may be prepared from menthone in one operation. A dry ethereal solution of the ketone is mixed with finely-powdered sodamide and heated until ammonia ceases to be evolved. A slight excess of an alkyl haloid is then added and the mixture again warmed until the precipitation of sodium haloid is complete. Finally, the ethereal solution is thoroughly washed with water, dried over anhydrous magnesium sulphate, and distilled. The residue is fractionated under reduced pressure. The alkylmenthones are colourless liquids insoluble in water and aqueous alkali hydroxide, but soluble in organic solvents. The following derivatives were prepared from a menthone which gave $\alpha_D -26^\circ 18'$ when examined in a layer of 1 decimetre length.

| | Boiling point. | α_D for $l=1$ decimetre. |
|--------------------|------------------------------|---------------------------------|
| Methylmenthone... | 96—97° under 13 mm. pressure | + 20° 18' |
| Ethylmenthone ... | 101—102 „ 13 „ | + 38° |
| Propylmenthone ... | 128—132 „ 19 „ | + 39° 20' |
| isoButylmenthone.. | 124—128 „ 10 „ | + 45° |
| isoAmylmenthone.. | 138—143 „ 10 „ | + 31° 48' |
| Allylmenthone ... | 134—137 „ 20 „ | + 25° 42' |

The inversion of rotatory power on passing from menthone to the alkyl derivatives is no doubt due to the action of alkali hydroxide on the original ketone; in fact, it was found that a dextrorotatory menthone, is obtained by acidifying the sodium salt prepared from the levorotatory variety. When an alkyl group is introduced into menthone a new asymmetric carbon atom is formed in the molecule; it is probable, therefore, that the above derivatives are not homogeneous, but consist of two or more optical isomerides. Sodium menthone reacts with aromatic aldehydes, and derivatives have been prepared from benzaldehyde and anisaldehyde. S. S.

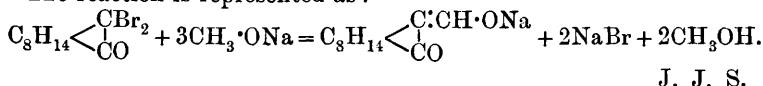
Preparation of Hydroxymethylene Compounds. JULIUS W. BRÜHL (*Ber.*, 1904, 37, 2069—2080).—Hydroxymethylene compounds may be obtained by the action of sodium methoxide free from methyl alcohol and prepared by the method recently described (active sodium methoxide, this vol., i, 545) on *o*-halogenated ketones.

A good yield (90 per cent.) of Claisen's hydroxymethylenecamphor may be obtained by dropping a benzene solution of *o*-dibromocamphor,

melting at 61° , into active sodium methoxide suspended in boiling benzene and kept well agitated. The same compound is obtained when *o*-bromo- or chloro-camphor is used, but the yield is not so good. Neither sodium methoxide containing methyl alcohol of crystallisation nor the commercial product can be employed in place of the so-called "active" form, and the *o*-halogenated derivatives of camphor cannot be replaced by isomerides, for instance, by β -dibromocamphor.

o-Bromomenthone under similar treatment yields hydroxymethylenementhone, $C_8H_{16} \begin{smallmatrix} \text{C:CH}\cdot\text{OH} \\ \diagup \\ \text{CO} \end{smallmatrix}$.

The reaction is represented as :



The Camphor Group. I and II. JULIUS W. BRÜHL [and MAX RÜDIGER] (*Ber.*, 1904, 37, 2156—2163; 2163—2178. Compare this vol., i, 139, 435, 436, and preceding abstract).—Iodine has no action on hydroxymethylenecamphor in indifferent solvents; in neutral aqueous solution,

α-iodoformylcamphor, $C_8H_{14} \begin{smallmatrix} \text{CI}\cdot\text{CHO} \\ \diagup \\ \text{CO} \end{smallmatrix}$, is precipitated, and crystal-

lises from acetic acid on addition of water in glistening, white leaflets, melting at 67 — 68° . It darkens on exposure to light, especially in solution. Cold concentrated hydrochloric acid dissolves it to a yellow solution, from which it is precipitated unaltered by water. Sodium

hypoiodite converts it into *αα*-di-iodocamphor, $C_8H_{14} \begin{smallmatrix} \text{Cl}_2 \\ \diagup \\ \text{CO} \end{smallmatrix}$, which

forms yellow leaflets resembling iodoform, but without odour, and melts at 108 — 109° . It is also obtained from hydroxymethylenecamphor and iodine in alkaline solution. Sodium methoxide decomposes its solution in benzene, forming camphor and a small quantity of hydroxymethylenecamphor.

α-Iodocamphor, $C_8H_{14} \begin{smallmatrix} \text{CHI} \\ \diagup \\ \text{CO} \end{smallmatrix}$, prepared by boiling iodoformyl-

camphor with sodium methoxide in methyl alcohol, crystallises from dilute alcohol in long, colourless needles and melts at 42 — 43° to a colourless liquid, which only becomes brown at 200° . It is quite stable at the ordinary temperature. Sodium methoxide in xylene forms principally hydroxymethylenecamphor. The same iodocamphor is obtained on boiling di-iodocamphor with potassium hydroxide.

On dissolving magnesium in an ethereal solution of *α*-bromocamphor, and adding iodine in small portions at a time, *α*-iodocamphor is obtained to the extent of 22 per cent., the remainder forming

the insoluble camphor magnesium bromide, $C_8H_{14} \begin{smallmatrix} \text{CH} \\ \diagup \\ \text{C}\cdot\text{O}\cdot\text{MgBr} \end{smallmatrix}$ (com-

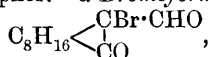
pare Malmgren, *Abstr.*, 1903, i, 710, and Brühl, this vol., i, 435). *α*-Chlorocamphor forms an insoluble magnesium compound, but no iodocamphor.

Sodamide reacts slowly with camphor, and the product absorbs

iodine, forming α -iodocamphor, but only to the extent of 15 per cent. An almost quantitative yield of iodocamphor is obtained by the action of sodium powder on an ethereal solution of camphor at the ordinary temperature and addition of iodine to the product. Some borneol and small quantities of condensation products are also obtained.

Bromine reacts with a neutral solution of hydroxymethylencamphor, forming α -bromoforylcamphor (compare Bishop, Claisen, and Sinclair, Abstr., 1895, i, 62; and Aschan and Brühl, Abstr., 1894, i, 613). In alkaline solution, α -bromocamphor is produced.

Hydroxymethylenementhone reacts with bromine in similar manner to hydroxymethylenecamphor. *α -Bromoforylmenthone*,



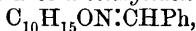
forms an unstable, slightly yellow oil, which could be neither distilled nor crystallised. *α -Bromomenthone*, $\text{C}_8\text{H}_{16} \begin{array}{l} \swarrow \text{CHBr} \\ \searrow \text{CO} \end{array}$, forms a colourless oil, rapidly becoming dark, and decomposing when heated under reduced pressure, but distilling in a current of steam.

C. H. D.

Metallo-organic Syntheses in the Camphor Group. GIUSEPPE ODDO (*Ber.*, 1904, 37, 1569—1572).—The process described by Malmgren (Abstr., 1903, i, 103, 710) for preparing dicamphor and dicamphorquinone from bromocamphor by the use of magnesium does not give a satisfactory yield, but by modifying the conditions a better result may be obtained with magnesium than with the old method in which sodium was used.

W. A. D.

α -Anhydropulegonehydroxylamine. FRIEDRICH W. SEMMLER (*Ber.*, 1904, 37, 2282—2289. Compare this vol., i, 437).—The action of benzaldehyde and sodium ethoxide on α -anhydropulegonehydroxylamine leads to the formation of a *benzylidene* derivative,



which melts at 105—106° and forms a *picrate*, $\text{C}_{17}\text{H}_{21}\text{ON} \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$, melting at 125—126°.

The tetrahydro-base forms a *thiocarbamide*, $\text{C}_{10}\text{H}_{20}\text{ON} \cdot \text{CS} \cdot \text{NHPh}$, which melts at 132°, effervesces when heated above its melting point, and then melts again at about 170°. The tetrahydro-base is also obtained by reducing pulegonehydroxylamine, or Beckmann and Pleissner's keto-amine (see Harries and Röder, Abstr., 1898, i, 573). The keto-amine distils unchanged at 99—100° under 10 mm. pressure.

G. Y.

Action of Paraformaldehyde on Sesquiterpenes. PIERRE GENVESSE (*Compt. rend.*, 1904, 138, 1228—1229).—Caryophyllene, clovene, and cadinene form compounds with formaldehyde which have alcoholic functions. The compound with caryophyllene, $\text{C}_{16}\text{H}_{26}\text{O}$, obtained by heating 1 mol. of caryophyllene with 1 mol. of trioxymethylene in a Pfungst tube at 180—200° for 10 hours, is a golden-yellow, slightly viscous liquid boiling at 177—178° under 15 mm.

pressure, has no odour, is soluble in alcohol, ether, or acetic acid, has a sp. gr. of 0.997 at 0°, $n_D - 7^{\circ}40'$ in a 4.93 per cent. chloroform solution at 21°, and $n_D 1.508$; it combines with one molecular proportion of bromine. The *acetate* boils at 185° under 15 mm. pressure, is soluble in ether, alcohol, or chloroform, has a sp. gr. 0.9969 at 0°, $n_D + 20^{\circ}33'$ in 11.7 per cent. chloroform solution at 18°, and $n_D 1.490$; it combines with 1 mol. of bromine.

The *compound* with clovene, $C_{16}H_{26}O$, boils at 170° under 12 mm. pressure, has a sp. gr. 1.001 at 0°, $n_D 1.5105$, $n_D - 7^{\circ}12'$ in 6.03 per cent. chloroform solution at 20°; it combines with 1 mol. of bromine. In each case, the molecular refraction points to one double linking in the molecule.

The *compound* with cadinene, $C_{16}H_{26}O$, boils at 180° under 15 mm. pressure, is an odourless, golden-yellow liquid, has a sp. gr. 0.993 at 0°, $n_D 1.521$, $n_D - 17^{\circ}54'$ in 7.6 per cent. chloroform solution at 20°; it combines with 2 mols. of bromine, and its molecular refraction points to the presence of two double linkings.

M. A. W.

Ethereal Oils. SCHIMMEL & Co. (*Chem. Centr.*, 1904, i, 1263—1265; from Schimmel's *Geschäftsber.*, April, 1904. Compare Abstr., 1902, i, 550; 1903, i, 185 and 569).—Apopin oil has been found by K. Keimazu (*J. Pharm. Soc. Japan*, August, 1903) to contain formaldehyde, *d*-pinene, and apopinol. *Apopinol*, $C_{10}H_{18}O$, is not identical with linalool; it boils at about 200°, and, on oxidation with chromic acid, yields citral. The oil is distinguished from camphor oil, which it very much resembles, by the presence of formaldehyde.

Bay oil, prepared from leaves from the Bermudas, differs from the distillate from the West Indian plant mainly in its higher sp. gr., which is 1.0301 at 15°, and its greater solubility in 80 per cent. alcohol. Cananga oil, obtained from fresh dried leaves of trees cultivated in Bangkok, had a sp. gr. 0.9200 at 15°, $[\alpha]_D - 51^{\circ}40'$, acid number 1.82, and ester number 34.17; it dissolved in 0.5 volume of 95 per cent. alcohol, but not in 10 volumes of 90 per cent. alcohol.

The determination of cinnamaldehyde in samples of the aldehyde or of Cassia oil by Hanus' method (Abstr., 1903, ii, 768) gives values which agree with those obtained by the sodium hydrogen sulphite method, but in the case of Ceylon cinnamon oil there is a difference which may amount to 8 per cent. between the results obtained by the two methods. Hanus' method is suitable for the determination of the aldehyde in cinnamon bark.

Oil of Cassia flowers, obtained by distilling the pomade prepared from the flowers of *Acacia farnesiana* with steam, removing the fatty acids and salicylic acid and again rectifying with steam, had a sp. gr. 1.0475 at 15°, $n_D 1.51331$ at 20°, and saponification number 176; it was optically inactive and contained methyl salicylate, *p*-cresol, benzaldehyde, benzyl alcohol, anisaldehyde, and a ketone, which has an odour similar to that of menthone, together probably also with cuminaldehyde. The oil of citronella recently supplied by the firm has been found to be adulterated with Russian petroleum. Since Bamber's method of detection is not quite accurate, the oil is tested for petroleum by treating it with 80 per cent. alcohol, and again after adding 5 per

cent. of petroleum; there should be no separation of oil in either case. Cypress oil, according to Soltmann, contains *d*-pinene, cypress camphor, furfuraldehyde, *d*-camphene, *d*-sylvestrene, *p*-cymene, sabinol (?), a terpene alcohol, which has the odour of roses, *d*-terpineol melting at 35°, and a ketone, which forms a semicarbazone melting at 177—178°. The *d*-terpineol is present in the form of an ester, which is probably the acetate.

A fraction obtained from an oil prepared from *Eucalyptus globulus* contained terpeneol and isoborneol, but not fenchyl alcohol. *iso*Amyl alcohol was found in the portions of the oil which boil at lower temperatures. A eucalyptus oil prepared from the same plant also yielded a sesquiterpene alcohol, $C_{15}H_{26}O$, which crystallises from 70 per cent. alcohol in colourless needles melting at 88.5°; it boils at 283° under 755 mm. pressure, and has $[\alpha]_D - 35.29'$ in chloroform solution. When heated with dehydrating agents, and especially with a 90 per cent. solution of formic acid, this alcohol yields a mixture of two sesquiterpenes, of which one boils at 247—248° under 748 mm. and at 102—103° under 6 mm. pressure; it has a sp. gr. 0.8956 at 15°, $n_D 1.49287$ at 20°, and $[\alpha]_D - 55.48'$. The other sesquiterpene boils at 265.5—266° under 755 mm. pressure, and has a sp. gr. 0.9236 at 15°, $n_D 1.50602$ at 20°, and $[\alpha]_D + 58.40'$.

The oil prepared from needles of the silver fir contains up to about 3 per cent. of lauraldehyde, and probably also decaldehyde. The semicarbazone of the former melts at 101.5—102.5°. The portion of the oil of *Reunion geranium*, which boils below the boiling point of citronella oil, consists mainly of menthone; amyl alcohol, *l*-pinene, linalool, and a small quantity of phellandrene were also detected. An apparently pure sample of ginger grass oil, which had a sp. gr. 0.9380 at 15°, $[\alpha]_D + 22.40'$, saponification number 24, and a saponification number for acetyl 166, did not give the phellandrene reaction directly although it contained phellandrene. The oil consisted mainly of geraniol and an unknown alcohol, $C_{10}H_{16}O$, which has an odour similar to that of linalool. This alcohol boils at 92—93° under 5 mm. pressure, has a sp. gr. 0.9503 at 15°, $[\alpha]_D + 8.40'$, $n_D 1.49735$ at 20°, and forms an acetate, which has the odour of curled mint and boils at 90—91° under 4 mm. pressure. The acetate has a sp. gr. 0.9725 at 15°, $[\alpha]_D - 4.30'$, and $n_D 1.47615$ at 20°. The acid obtained by saponifying the oil melts at 106—107° and forms a very sparingly soluble silver salt, which contains 38.9 per cent. of silver.

The fraction of camphor oil boiling at 210—220° contains borneol. Butyric acid has been detected in French oil of lavender, and the neutral products of the saponification of the oil probably contain *iso*amyl alcohol. The oil prepared from *Monodora myristica* consists chiefly of phellandrene; it has a sp. gr. 0.859 at 15°, $[\alpha]_D - 117.40'$, acid number 1.36, and ester number 3.4. In a sample of oil of patchouli, which had a sp. gr. 0.9769 at 15°, $[\alpha]_D - 55.45'$, acid number 2.2, and saponification number 4.2, benzaldehyde, eugenol, and cinnamaldehyde were detected together with an alcohol, a ketone, and two bases which have not yet been identified. The semicarbazone of the ketone melted at 134—135°. No evidence as to the nature of the odoriferous principle of the oil was obtained, and cadinene did not appear to be present.

Patchoulene, prepared from the oil by means of formic acid, boils at 255—256° and has a sp. gr. 0.9334 at 15° and $[\alpha]_D - 36.52'$. Pimento oil contains cineol, *l*-phellandrene, caryophellene, eugenol, eugenol methyl ether, and palmitic acid, together probably also with small quantities of terpene alcohols.

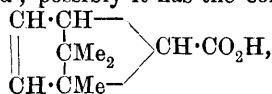
In addition to several South Australian eucalyptus oils and cajeput oils, the following new oils are described. Yomugi oil is more probably an oil from a kind of *Artemisia* or *chrysanthemum*; it has a sp. gr. 0.9126 at 15°, $[\alpha]_D - 18.15'$, acid number 1.32, and ester number 16.19. Kuromoji oil is pale yellow and contains cineol, and probably also linalool; it has a sp. gr. 0.8947 at 15°, $[\alpha]_D - 14.29'$, and ester number 29.87. May oil from Porto Rico, prepared from *Calyptranthes paniculata* (*Myrtaceæ*), contained 62.5 per cent. of citral, and had a sp. gr. 0.9509 at 15° and $[\alpha]_D - 1.52'$. A pale yellow oil from *Mentha citrata* (Bergamot mint) from Florida, had a sp. gr. 0.8826 at 15°, $[\alpha]_D - 5.35'$, and an ester number 31.28, corresponding with 10.95 per cent. of linalyl acetate. A bright yellow oil from *Hyptis spicata* (*Mesophaerum spicatum*; *Labiatae*), also from Florida, had a sp. gr. 0.915 at 15°, $[\alpha]_D - 27.25'$, acid number 2.17, and ester number 4.35; it probably contained small quantities of menthone or pulegone. A green oil from *Ambrosia artemisiæfolia* had a sp. gr. 0.876 at 15°, $[\alpha]_D - 1^\circ$, and ester number 7.94. A pale yellow oil from *Eupatorium capillifolium* had a sp. gr. 0.926 at 15°, $[\alpha]_D + 18.38'$, and an ester number 7.11. The pale greenish-blue colour of an Australian *essence de Bruyère* was found to be due to the presence of copper; the essence had a sp. gr. 0.8587 at 15° and $[\alpha]_D + 2.44'$. The oil distilled from the wood of *Erythroxylon monogynum* formed a gummy, crystalline mass, which had a pleasant odour. It contained a compound $C_{20}H_{32}O$ of an alcoholic character, which crystallises from light petroleum in needles and melts at 117—118°; the acetate melts at 72—73°. E. W. W.

Essential Oil of *Artemisia Herba Alba* of Algeria. EMILIEN GRIMAL (*Bull. Soc. chim.*, 1904, [iii], 31, 694—697).—The fresh plant, when steam-distilled previous to the flowering stage, furnishes 0.3 per cent. of a yellowish-green oil with a pleasant, aromatic odour and a camphoraceous, slightly bitter taste. It is readily soluble in 80 per cent. alcohol and less so in 70 and 60 per cent. alcohols, has a sp. gr. 0.9456 at 15°, n_D 1.47274 at 20°, and $[\alpha]_D - 15.30'$ at 20°. The acid number is 6.46, and saponification numbers before and after acetylation 89.23 and 135.38 respectively, corresponding with 24.48 per cent. of combined alcohols and 12.65 per cent. of free alcohols respectively.

The oil distilled between 35° and 135°, and the proportions and principal physical properties of the nine fractions collected are tabulated in the original. The oil is found to contain *l*-camphene, cineol, *l*-camphor, an alcohol, furnishing on oxidation with chromic acid a product having the odour of citral, and esters of octoic and decoic acids. T. A. H.

Essential Oil of Laurel Leaves. HERMANN THOMS and B. MOLLE (*Arch. Pharm.*, 1904, 242, 161—181).—The oil examined amounted to 2.4 kilos. and had sp. gr. 0.9215 at 17°, $n_D - 15.95^\circ$ at 17° in a 100 mm. tube, acid number 2.74, saponification number 49.8. The

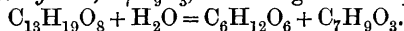
free acids consisted of acetic, *isobutyric*, and (*iso*?) valeric. About 1·7 per cent. of free eugenol was present, and about 0·4 per cent. in the form of esters. The acids obtained by hydrolysing the oil with alcoholic potassium hydroxide consisted mainly of acetic acid; the other volatile acids present were probably valeric and hexoic, approximately in the proportion 2:3. A monobasic acid, $C_{10}H_{14}O_2$, insoluble in water, was also obtained in yield of 0·07 per cent., and its *silver*, *lead*, and *copper* salts were analysed; this acid melts at 146—147°, takes up 2Br, and decolorises permanganate solution energetically in the cold; possibly it has the constitution



and probably it is formed through the action of the potassium hydroxide on the oil. Pinene (compare Wallach, Abstr., 1889, 1072) can no longer be detected in the oil after the treatment with alkali.

The oil remaining after the free acids, phenols, and esters had been removed was fractionated. Cineol, $C_{10}H_{18}O$, was obtained from it in yield equal to 50 per cent. of the original oil; it can be purified by means of the crystalline compound that it forms with arsenic (as with phosphoric) acid; this compound is decomposed by water into its constituents. From the fractions boiling between 212° and 230°, geraniol was isolated; these fractions yielded terpinene when boiled with 50 per cent. sulphuric acid, and terpene hydrate when treated with acid of 5 per cent. strength or more. The fractions of still higher boiling point contain oxygen; probably they contain a sesquiterpene alcohol as well as a sesquiterpene. These fractions, and also the original oil, give an intense blue coloration when they are dissolved in glacial acetic acid and bromine vapour is blown over the surface of the solution. Methylchavicol could not be detected in the oil. C. F. B.

Aucubin. ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1904, 138, 1114—1116. Compare Abstr., 1902, i, 634).—The glucoside aucubin, $C_{13}H_{19}O_8 \cdot H_2O$, found together with sucrose, not only in the seeds, but also in the leaves, stem, and root of *Aucuba japonica*, is soluble in water, or ethyl or methyl alcohol, 100 parts of the solvent at 20—22° dissolving 35·6 parts in the case of water, 1·1 parts in the case of 95 per cent. alcohol, 7·7 in the case of 85 per cent. alcohol, and 13·8 in the case of methyl alcohol free from acetone; it is insoluble in ether or chloroform, and crystallises with one molecular proportion of water, which it loses on prolonged heating at 115—120°. Aucubin is readily hydrolysed by very dilute acids, or by a ferment identical with emulsin found in the leaves of the plant forming dextrose and *aucubigenin*, $C_7H_9O_3$, according to the equation



Both aucubin and aucubigenin are without toxic action.

M. A. W.

The Glucoside Robinin. NICOLAI A. WALJASCHKO (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 421—438. Compare Schmidt and Waljaschko, Abstr., 1901, i, 602).—The robinin examined was

obtained from white azaleas (*Robinia pseudacacia* L.), by extracting the flowers either when fresh with water or when dried with alcohol. Its composition is $C_{33}H_{40}O_{19} \cdot 7\frac{1}{2}H_2O$; $7H_2O$ are lost readily, and the remaining $\frac{1}{2}H_2O$ at 110° . By means of dilute mineral acids, robinin is hydrolysed, yielding galactose (1 mol.), rhamnose (2 mols.), and a yellow colouring matter, to which the author gives the name robigenin: $C_{33}H_{40}O_{19} + 3H_2O = C_6H_{12}O_6 + 2C_6H_{12}O_5 + C_{15}H_{10}O_6$. Robigenin yields crystals, $C_{15}H_{10}O_6 \cdot H_2O$, which lose their water at 130° and melt at 270° .
T. H. P.

Triphenylmethane Dyes, Stable towards Alkalis. CHARLES LAUTH (*Compt. rend.*, 1904, 138, 1220—1221).—By the action of acetyl chloride, acetic anhydride, or benzenesulphonic chloride on the leuco-bases obtained by reducing the condensation products of *m*-nitrobenzaldehyde and dimethyl- or diethyl-aniline, the hydrogen of the NH_2 group is replaced by an acetyl or benzenesulphonyl radicle, and the resulting compounds on sulphonation and oxidation yield *blue* dyes analogous to *patent blue* in purity of tint and stability towards alkalis, the substituted NH_2 group in the new series of compounds apparently playing the same rôle as the hydroxyl in the original series.

M. A. W.

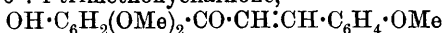
Black Sulphur Dye from *m*-Phenylenediamine. KALLE & Co. (D.R.-P. 150834).—A black dye is obtained by fusing *m*-phenylenediamine with *o*-nitrophenol, sodium sulphide, and sulphur, the latter substances being in the proportion to form sodium tetrasulphide. It is not possible to replace the *o*-nitrophenol by *o*-aminophenol.

C. H. D.

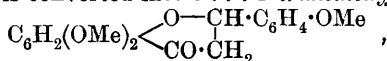
Lactucon. FRIEDRICH SPERLING (*Chem. Centr.*, 1904, i, 1162; from *Zeit. Oesterr. Apoth.-Ver.*, 42, 249—252).—*Lactucon*, $C_{23}H_{36}O_2$, prepared by extracting *Lactucarium germanicum* with light petroleum, is a white, odourless substance which crystallises from hot alcohol in colourless needles and melts at 184° . It is readily soluble in ether, benzene, chloroform, light petroleum, carbon disulphide, or hot alcohol, but very sparingly so in cold alcohol and insoluble in water. By the action of a boiling 1 per cent. solution of potassium hydroxide in alcohol, lactucon yields acetic acid and lactucol. *Lactucol*, $C_{21}H_{33} \cdot OH$, crystallises from alcohol in needles and melts at 154.5° . The bromine compound, $C_{23}H_{36}O_2Br_2$, prepared by the action of bromine dissolved in carbon disulphide on lactucol, crystallises in yellow needles and decomposes on heating. Lactucon is the acetyl derivative of lactucol.

E. W. W.

Synthesis of Kaempferol. STANISLAUS VON KOSTANECKI, VICTOR LAMPE, and JOSEF TAMBOR (*Ber.*, 1904, 37, 2096—2099).—When 2'-hydroxy-4' : 6' : 4-trimethoxychalkone,



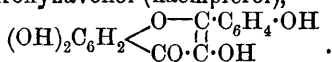
(compare this vol., i, 426), is boiled in alcoholic solution with dilute sulphuric acid, it is converted into 5 : 7 : 4'-trimethoxyflavanone,



which separates from alcohol in white pyramids and melts at 125°. It forms a yellow solution with alcoholic sodium hydroxide. The *isonitroso*-derivative, $C_6H_2(OMe)_2 \begin{smallmatrix} O-CH \cdot C_6H_4 \cdot OMe \\ | \\ CO \cdot C \cdot N \cdot OH \end{smallmatrix}$, prepared by the action

of *amyl nitrite* on the preceding compound, separates from alcohol in pale yellow needles, which melt and decompose at 189–190°. When boiled with dilute sulphuric acid, it forms 5:7:4'-*trimethoxyflavonol*, $C_6H_2(OMe)_2 \begin{smallmatrix} O-C \cdot C_6H_4 \cdot OMe \\ | \\ CO \cdot C \cdot OH \end{smallmatrix}$, which crystallises from alcohol in

pale yellow needles, grouped in rosettes, and melts at 151–152°. Its *sodium* salt is intensely yellow; its *acetyl* derivative separates from dilute alcohol in white needles and melts at 190–191°. When 5:7:4'-*trimethoxyflavonol* is heated with strong hydriodic acid, it forms 5:7:4'-*trihydroxyflavonol* (*kaempferol*),



Acetyl-5:7:4'-*trimethoxyflavonol*, when warmed with hydriodic acid, gave 5:7:4'-*trihydroxyflavonol*, melting at 275°, whilst Gordin and Kostanecki give 271° as the melting point of naturally occurring *kaempferol*.

Acetyl-5:7:4'-*triacetoxyflavonol* forms prismatic needles and melts at 181. A. McK.

5:7-Dihydroxy-2-methylchromone E. JOCHUM and STANISLAUS VON KOSTANECKI (*Ber.*, 1904, 37, 2099–2101. Compare Kostanecki and de Wildt, *Abstr.*, 1902, i, 303).—2:4:6-*Trimethoxy-acetylaceto-phenone*, $C_6H_2(OMe)_3 \cdot CO \cdot CH_2 \cdot COMe$, obtained by condensing phlor-acetophenone dimethyl ether with ethyl acetate by means of sodium, separates from dilute alcohol in colourless prisms and melts at 94–95°; its alcoholic solution gives a red coloration with ferric chloride. When boiled with strong hydriodic acid, it forms

5:7-dihydroxy-2-methylchromone, $C_6H_2(OH)_2 \begin{smallmatrix} O-CMe \\ | \\ CO \cdot CH \end{smallmatrix}$, which separates from alcohol in glistening, tiny plates and melts at 290°. Its solution in concentrated sulphuric acid is colourless and does not exhibit fluorescence. Its *acetyl* derivative separates from dilute alcohol in white needles and melts at 149°. A. McK.

Synthesis of 6:2'-Dihydroxyflavonol. A. KATSCHALOWSKY and STANISLAUS VON KOSTANECKI (*Ber.*, 1904, 37, 2346–2351).—The tinctorial properties of 6:2'-dihydroxyflavonol are contrasted with those of 6:3'-dihydroxyflavonol (*this vol.*, i, 441) and 6:4'-dihydroxyflavonol (*this vol.*, i, 442). With respect to the theory of dyes, the 2':3-position in the flavone group is comparable with the *peri*-position in the naphthalene series, and is designated by the authors as the *anchi*-position.

6:2'-Dimethoxyflavanone, $OMe \cdot C_6H_3 \begin{smallmatrix} O-CH \cdot C_6H_4 \cdot OMe \\ | \\ CO \cdot CH_2 \end{smallmatrix}$, prepared by adding sodium hydroxide to an alcoholic solution of quinaceto-phenone monomethyl ether (*this vol.*, i, 440) and salicylaldehyde

methyl ether, forms colourless pyramids and melts at 120°; its solution in concentrated sulphuric acid is red. The *isonitroso*-derivative, $\text{OMe} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} - \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe} \\ \text{CO} \cdot \text{C} \cdot \text{N} \cdot \text{OH} \end{smallmatrix}$, prepared by the action of amyl nitrite on the preceding compound, separates from alcohol in yellow needles and melts and decomposes at 164—166°.

6 : 2'-*Dimethoxyflavonol*, $\text{OMe} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} - \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe} \\ \text{CO} \cdot \text{C} \cdot \text{OH} \end{smallmatrix}$, prepared by hydrolysis of the preceding oxime with sulphuric acid, separates from alcohol in colourless prisms and melts at 187—188°; it is insoluble in cold sodium hydroxide, but on warming it dissolves to a yellow solution, from which the yellow sodium salt separates on cooling. The *acetyl* derivative separates from dilute alcohol in colourless, prismatic needles and melts at 121—122°.

6 : 2'-*Dihydroxyflavonol*, $\text{OH} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} - \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OH} \\ \text{CO} \cdot \text{C} \cdot \text{OH} \end{smallmatrix}$, prepared by the action of hydriodic acid on the dimethyl ether, crystallises from dilute alcohol in pale yellow needles and melts at 242—243°. It is easily soluble in dilute sodium hydroxide. A. McK.

3-Alkyl-substituted Benzopyranols. CARL BÜLOW and IVO DEIGLMAYR (*Ber.*, 1904, 37, 1791—1800. Compare Bülow, *Abstr.*, 1903, i, 272).—Further evidence is now submitted to prove that the condensation product formed from methylacetylacetone and resorcinol is 7-hydroxy-2 : 3-dimethyl-4-methylene-1 : 4-benzopyranol. The general nature of the reaction is also indicated by the substitution of orcinol (1 : 3 : 4-trihydroxybenzene), pyrogallol, and phloroglucinol respectively for resorcinol (*m*-dihydroxybenzene).

7-Hydroxy-2 : 3-dimethyl-4-methylene-1 : 4-benzopyranol, prepared by adding an excess of sodium acetate to the hydrochloride previously described (*loc. cit.*), separates from dilute alcohol in microscopic, brick-red crystals; it forms, with concentrated sulphuric acid, a yellow solution, which, when diluted, exhibits bluish-violet fluorescence. Its *acetyl* derivative is amorphous. The constitution of 7-hydroxy-2 : 3-dimethyl-4-methylene-1 : 4-benzopyranol was proved by the isolation of methyl ethyl ketone, resacetophenone, resorcinol, and acetic acid as products resulting from the action of a concentrated aqueous solution of potassium hydroxide on the hydrochloride.

7-Hydroxy-2 : 3 : 5-trimethyl-4-methylene-1 : 4-benzopyranol *hydrochloride*, prepared by condensing methylacetylacetone with orcinol, forms lemon-yellow needles, which melt and decompose at 192—196°. With sulphuric acid, it forms a yellow solution which exhibits a faint blue fluorescence. The corresponding *picrate* melts and decomposes at 180—185°.

6 : 7-Dihydroxy-2 : 3-dimethyl-4-methylene-1 : 4-benzopyranol *hydrochloride*, prepared from methylacetylacetone and 1 : 3 : 4-trihydroxybenzene, separates from dilute hydrochloric acid in bright yellow, silky needles which crystallise with $2\frac{1}{2}\text{H}_2\text{O}$ and HCl ; it melts and decomposes at 255—265°, and its solutions are feebly fluorescent. The corresponding *picrate* was also prepared.

7 : 8-Dihydroxy-2 : 3-dimethyl-4-methylene-1 : 4-benzopyranol hydrochloride, prepared from methylacetylacetone and pyrogallol, crystallises with $1\text{H}_2\text{O}$ and forms orange-red needles, which, with concentrated sulphuric acid, form a lemon-yellow solution, with sodium hydroxide a bluish-black solution, and with ammonia a carmine-red solution. The corresponding *picrate* melts and decomposes at $195-200^\circ$. The free base forms a dark carmine-red powder; its *diacetyl* derivative softens at 135° and melts completely at 148° .

5 : 7-Dihydroxy-2 : 3-dimethyl-4-methylene-1 : 4-benzopyranol hydrochloride, prepared from methylacetylacetone and phloroglucinol, crystallises with 1HCl and $1\text{H}_2\text{O}$. It forms fine, brownish-yellow needles. Its solution in concentrated sulphuric acid is bright yellow. The corresponding *picrate* was also prepared. The free base is a yellow, amorphous powder; its *diacetyl* derivative is a green, amorphous powder. A. McK.

New Condensation Derivatives of Benzoylphthalylacetone. CARL BÜLOW [with BERTHOLD KOCH] (*Ber.*, 1904, 37, 1964—1971).—3-Benzoyl-7-hydroxy-4-methylene-1 : 4-benzopyranol-2-phenyl-o-carboxylic acid, $\text{OH}\cdot\text{C}\cdot\text{CH}=\text{C}\cdot\text{O}-\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, obtained by passing dry

hydrogen chloride through a cold solution of phthalylbenzoylacetone and resorcinol in glacial acetic acid, separates from the solvent in microscopic, golden crystals and melts at 245° ; on acetylation, it gives the corresponding 7-acetoxy-derivative, $\text{C}_{26}\text{H}_{18}\text{O}_6$, which forms slender, white needles and melts at 148° . When the carboxylic acid is heated with 10 per cent. aqueous potassium hydroxide, it gives acetophenone, resorcinol, phthalic acid, and resacetophenone; it is probable that resacetophenone and benzoylphthalylmethane are the primary products and that they undergo further decomposition.

3-Benzoyl-5 : 7-dihydroxy-4-methylene-1 : 4-benzopyranol-2-phenyl-o-carboxylic acid, $\text{C}_{24}\text{H}_{16}\text{O}_6$, prepared by condensing benzoylphthalylacetone with phloroglucinol, crystallises from glacial acetic acid and melts and decomposes at 263° ; its *diacetyl* derivative, $\text{C}_{28}\text{H}_{20}\text{O}_8$, melts and decomposes at 189° .

Alternative formulæ for the foregoing pyranol derivatives are suggested and the mechanism of the condensation discussed.

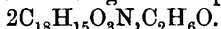
W. A. D.

The Indophenine Reaction. LUDWIG STORCH (*Ber.*, 1904, 37, 1961).—The indophenine reaction, although not given by isatin with benzene containing thiophen in presence of pure sulphuric acid, is at once produced on gently warming the mixture; that the addition of a solution of ferric chloride or potassium dichromate simply develops the heat necessary for the interaction is shown by the fact that water produces the same effect (compare Bauer, this vol., i, 519).

W. A. D.

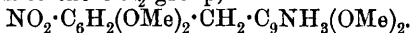
Condensation Products from Thalline and Cotarnine. CARL RENZ and MARTIN HOFFMANN (*Ber.*, 1904, 37, 1962—1964).—Thalline condenses with phthalic anhydride (1 mol.) with elimination of H_2O to form a compound, $\text{C}_{18}\text{H}_{15}\text{O}_8\text{N}$, which, after being boiled with alcohol

and recrystallised from glacial acetic acid, separates in white, lustrous crystals melting at 239° and having the composition



Cotarnine, on being heated with vanillin at 100 — 110° , gives a *product*, the *hydrochloride*, $\text{C}_{10}\text{H}_{17}\text{O}_4\text{N}, \text{HCl}, \text{H}_2\text{O}$, of which, crystallises from alcohol in golden-coloured needles and melts at 198° ; the corresponding base could not be obtained. With catechuic aldehyde, cotarnine condenses giving a *base*, the *hydrochloride*, $\text{C}_{19}\text{H}_{19}\text{O}_6\text{N}, \text{HCl}$, of which melts at 159 — 160° .
W. A. D.

Conversion of Papaverine into an *iso*Quinoline Base derived from Phenanthrene. ROBERT PSCHORR [with M. STÄHLIN and M. SILBERBACH] (*Ber.*, 1904, 37, 1926—1942).—Hesse's nitropapaverine (*Annalen*, 1872, Suppl. 8, 292) is proved to contain the nitro-group in the ortho-position to the CH_2 group,



It crystallises from ethyl acetate in long, colourless needles, becoming yellow in air, melts at 186 — 187° (corr.), and dissolves in 100 — 110 parts of boiling alcohol, 40 parts of ethyl acetate, 3 parts of chloroform, or 10 parts of xylene. The *methiodide*, $\text{C}_{21}\text{H}_{23}\text{O}_6\text{N}_2\text{I}$, crystallises from water in thick, yellow prisms, melts at 225° (corr.), and decomposes at 235° ; the *methobromide* forms bright yellow prisms, darkening at 210° and melting and decomposing at 227° (corr.). The *methomethyl sulphate* forms bright yellow prisms and melts and decomposes at 238° (corr.), and reacts with potassium chloride to form the *methochloride* melting at 212° (corr.).

Potassium permanganate oxidises nitropapaverine methiodide to 6-nitroveratric acid (6-nitro-3:4-dimethoxybenzene-1-carboxylic acid). Boiling potassium hydroxide forms 6-nitrohomoveratrole (6-nitro-3:4-dimethoxy-1-methylbenzene) and *dimethoxyisoquinolone*, $\text{C}_{12}\text{H}_{13}\text{O}_3\text{N}$, which crystallises from benzene in thick, colourless prisms, sinters at 102° , and melts at 107° ; its *hydrochloride* forms silky needles and melts at 186 — 187° (corr.).

Stannous chloride reduces nitropapaverine to *aminopapaverine*, forming slender, felted needles containing alcohol and melting at 116° ; after removal of the alcohol by heating or prolonged drying, it sinters at 130° and melts at 143° (corr.). The *acetyl* derivative crystallises with 1 mol. of benzene and melts at 125° ; when dried, it melts at 162° (corr.).

Diazopapaverine, $\text{C}_{20}\text{H}_{19}\text{O}_4\text{N}_3$, prepared by adding sodium nitrite to a solution of aminopapaverine in cold concentrated sulphuric acid, crystallises from alcohol in colourless tablets and melts at 281° (corr.). The *methiodide*, $\text{C}_{21}\text{H}_{23}\text{O}_4\text{N}_3\text{I}, \text{H}_2\text{O}$, forms slender, yellow needles, and after drying sinters at 185° and melts and decomposes at 198° (corr.). The *methomethyl sulphate* forms star-shaped groups of yellow needles, sinters at 163° , and melts at 168 — 169° (corr.). Potassium hydroxide converts diazopapaverine methiodide into an orange compound, melting at 170° , dissolving readily in water, and containing no iodine (compare Decker and Klauser, this vol., i, 338).

Nitropapaveraldine, prepared by heating papaveraldine (Goldschmidt, *Abstr.*, 1886, 478) with nitric acid, crystallises from alcohol in slender, yellow needles and melts at 199 — 200° (corr.). The same compound is

obtained on oxidising nitropapaverine in boiling glacial acetic acid solution with sodium dichromate. Stannous chloride reduces it, forming a mixture of anthranilopapaverine and aminopapaveraldine. *Anthranilopapaverine*, $C_{20}H_{18}O_5N_2$, crystallises from alcohol in slightly yellow, slender needles, sinters at 235° and melts at $244\text{--}245^\circ$ (corr.). It dissolves readily in chloroform, very sparingly in alcohol, acetone, or ethyl acetate, and is insoluble in water or ether. It is probably an internal anhydride resembling methylantranil and containing the

group $\text{:C} \begin{array}{c} \diagup \text{O} \diagdown \end{array} \text{N}$. Concentrated sulphuric acid converts it into a *sulphonic acid* melting at 233° .

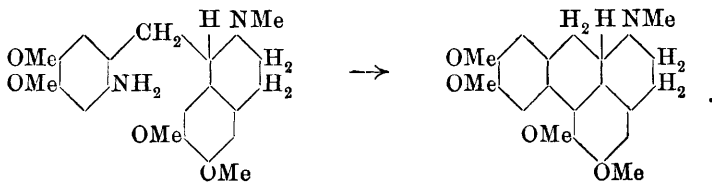
Aminopapaveraldine, $C_{20}H_{20}O_5N_2$, obtained from the filtrate from the above compound, or by reducing nitropapaveraldine with ammonium sulphide, crystallises from alcohol in bright yellow needles and melts at $171\text{--}172^\circ$ (corr.), dissolving readily in organic solvents, sparingly in hot water. Dilute acids dissolve it to intensely red solutions, concentrated acids form bright yellowish-green solutions, becoming red on dilution.

Diazopapaveraldine sulphate, $C_{20}H_{19}O_9N_3S$, crystallises from warm water in microscopic, orange needles, darkens at 120° , and melts at 225° (corr.) to a dark green liquid.

Amino-N-methyltetrahydropapaverine, $C_{21}H_{28}O_4N_2$, prepared by reducing nitropapaverine methochloride with tin and hydrochloric acid, crystallises from ethyl acetate or methyl alcohol in stellar groups of needles, melts at 145° (corr.), and dissolves readily in chloroform, very sparingly in ether. The hydrochloride, sulphate, and nitrate dissolve readily in water, slightly acid solutions give an intense, permanent, blue coloration with ferric chloride. The base may be regarded as *dl*-aminolaudanosiine (compare Pictet and Athanasescu, Abstr., 1900, i, 685).

When a smaller quantity of hydrochloric acid is employed in the reduction, *aminopapaverine methochloride hydrochloride*, $C_{21}H_{26}O_4N_2Cl_2$, is obtained, crystallising in colourless tablets and melting at 200° (corr.). *Aminopapaverine methochloride* forms slightly yellow needles and melts at 147° (corr.).

When copper powder is added to a diazotised solution of *N*-methyltetrahydroaminopapaverine, a syrupy liquid is obtained, from which crystals of *phenanthreno-N-methyltetrahydropapaverine methiodide*, $C_{22}H_{28}O_4NI$, are obtained by adding methyl iodide and extracting with acetone. The methiodide crystallises from alcohol in faintly yellow prisms and melts at 215° (corr.). Its formation takes place according to the following scheme:



C. H. D.

Lupinidine and Sparteine. RICHARD WILLSTÄTTER and WILHELM MARX (*Ber.*, 1904, 37, 2351—2357).—Willstätter and Fourneau have shown (*Abstr.*, 1902, i, 557) that lupinine and lupinidine are not identical, the latter having the high boiling point 311—314°, and that lupinidine resembles sparteine in many properties.

Lupinidine, $C_{15}H_{26}N_2$, was prepared from the seeds of *Lupinus luteus*, the amount obtained after removal of lupinine by treatment with light petroleum being 0.23 per cent. of the seeds used. It boils at 180.5° under 18 mm. pressure and has the sp. gr. 1.034 at 0° and 1.023 at 20°. The data in the literature respecting the boiling point of sparteine are discordant; according to Peratoner, sparteine boils at 185—190° under 18 mm. pressure. The authors find for lupinidine $[\alpha]_D -5.96^\circ$ at 20° and $[\alpha]_D -16.41^\circ$ at 21° in 99 per cent. alcohol, where $c=14.206$; whilst, according to Moureu and Valeur (*Abstr.*, 1903, i, 717), the corresponding values for sparteine are -5.41° and -16.42° ($c=10-15$). Lupinidine and sparteine also possess identical solubilities, since when their aqueous solutions, saturated at 18°, are precipitated by picric acid, the amounts precipitated from the respective solutions being practically identical. The platinichlorides of sparteine and lupinidine are identical; both begin to blacken at 239°, and melt with decomposition at 243.5°. *Sparteine hydrogen sulphate* separates in prisms, which melt and decompose at 232°. A. McK.

Cevadine [Veratrine]. II. MARTIN FREUND [and EDMUND SPEYER] (*Ber.*, 1904, 37, 1946—1957. Compare Freund and Schwarz, *Abstr.*, 1899, i, 464).—Only one acyl group can be introduced into veratrine; cevine, on the other hand, allows of the introduction of two acyl groups.

Benzoylveratrine benzoate, $C_{32}H_{48}O_9NBz, C_6H_5 \cdot CO_2H, H_2O$, prepared by heating veratrine with benzoic anhydride at 105—107°, crystallises from dilute alcohol in small, white needles, becomes anhydrous at 120°, and melts at 150—155°. It dissolves readily in alcohol, benzene, or acetone, sparingly in ether, very slightly in water. *Benzoylveratrine*, precipitated by ammonia from the alcoholic solution of the benzoate, crystallises from alcohol in small, triangular prisms and melts at 255°. The *hydrochloride*, $C_{39}H_{53}O_{10}N, HCl, H_2O$, forms small, white needles; the *hydriodide* forms yellowish-white needles and melts at 220—222°; the *nitrate* forms small, white needles and melts at 194—195°.

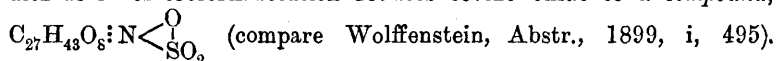
Acetylveratrine, $C_{32}H_{48}O_9NAc$, melts at 182° to a viscous mass, then solidifies, and again melts at 234° to a yellow liquid. The *hydrochloride* is a brittle mass dissolving readily in water.

Dibenzoylcevine benzoate, $C_{41}H_{51}O_{10}N, C_6H_5 \cdot CO_2H$, forms microscopic prisms and melts at 193—195°. Ammonia precipitates *dibenzoylcevine*, crystallising in large tablets and melting at 195—196°. The *hydrochloride* forms small, prismatic tablets containing H_2O , sinters at 223° and melts at 227°. The *nitrate* forms small rods and melts at about 262°; the amorphous *acetate* melts at 170°.

Diacetylcevine melts at 190°.

Hydrogen peroxide oxidises cevine to *cevine oxide*, $C_{27}H_{43}O_9N$, crystallising from dilute alcohol in white rods and melting at 275—278°. The *hydrochloride* is amorphous and decomposes at about 208—210°.

On the addition of alkali to the solution, the base is not obtained until after warming, when it separates in a pure state. The *aurichloride* is amorphous and melts and decomposes at 185°. Sulphur dioxide in chloroform solution reduces cevine oxide to a compound,



Barium chloride reconverts this into cevine. The formation of the oxide indicates that cevine is a tertiary base, and probably contains a double ring-system, as in the case of hydroberberine.

The physiological action of the compounds described is set forth in detail by Heinz. C. H. D.

Action of Sulphuryl Chloride on Pyrrole. IV. GIROLAMO MAZZARA and A. BORGO (*Gazzetta*, 1904, 34, i, 253—262. Compare Abstr., 1902, i, 820; 1903, i, 51 and 274).—2:3:5-*Trichloropyrrole*, $\text{C}_4\text{NH}_2\text{Cl}_3$, prepared by gradually adding sulphuryl chloride ($3\frac{1}{2}$ mols.) to an ethereal solution of pyrrole (1 mol.), kept cool by means of ice, is obtained as a pale yellow oil which could not be purified; it blackens under the action of light and its vapours irritate the eyes. On treatment, in methyl-alcoholic solution, with methyl iodide and potassium hydroxide, it yields 2:3:5-*trichloro-1-methylpyrrole*, $\text{C}_4\text{NHMeCl}_3$, which is a colourless oil, heavier than water; it darkens but little in the light and its vapour attacks the eyes.

Chloromaleic methylimide, $\text{NMe} \begin{array}{c} \text{CO}\cdot\text{CH} \\ \diagup \quad \diagdown \\ \text{CO}\cdot\text{CCl} \end{array}$, prepared by oxidising 2:3:5-trichloro-1-methylpyrrole by means of concentrated nitric acid, crystallises from light petroleum in white, nacreous plates melting at 79°; it is volatile in a current of steam, and its vapour has a very pungent odour and strongly attacks the eyes.

2:3:4:5-*Tetrachloro-1-methylpyrrole*, C_4NMeCl_4 , prepared from the tetrachloropyrrole obtained in small quantity by the action of $3\frac{1}{2}$ mols. of sulphuryl chloride on 1 mol. of pyrrole, crystallises from light petroleum in short, stout needles, which melt at 118—119° and dissolve in concentrated sulphuric acid yielding a pale rose-coloured solution. On oxidation with concentrated nitric acid, this compound yields *dichloromaleic methylimide*, $\text{NMe} \begin{array}{c} \text{CO}\cdot\text{CCl} \\ \diagup \quad \diagdown \\ \text{CO}\cdot\text{CCl} \end{array}$,

which separates from alcohol in large, shining plates melting at 86°; it is volatile in a current of steam and its vapour irritates the eyes.

T. H. P.

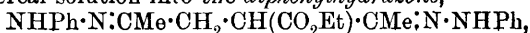
Action of Hydrazine on Ethyl $\alpha\beta$ -Diacetylpropionate (Ethyl 2:5-Hexadione-3-carboxylate). G. KORSCHUN (*Ber.*, 1904, 37, 2183—2192).—Ethyl 2:5-hexadione-3-carboxylate reacts vigorously with hydrazine in alcoholic solution, forming ethyl 3:6-dimethyl-4:5-dihydropyridazine-4-carboxylate and ethyl 3:6-dimethylpyridazine-4-carboxylate, which have been obtained by Bülow (Abstr., 1903, i, 196) and Paal and Ueber (Abstr., 1903, i, 290) from the dicarboxylate. *Ethyl 2:5-dimethylfuran-3-carboxylate*, $\text{C}_9\text{H}_{12}\text{O}_3$, is produced at the same time, but is not readily obtained pure. It is identified by hydrolysis to the corresponding acid.

An ester of high boiling point is also produced, and is possibly ethyl 1-bis-2:5-dimethylpyrrole-3-carboxylate. The acid obtained by hydrolysis is crystalline and melts and decomposes above 360°.

Hydrazine acetate reacts with ethyl hexadionecarboxylate to form *ethyl 2:5-dimethylpyrrole-3-carboxylate*, $C_9H_{14}O_2N_2$, which crystallises from hot water and melts at 87–88°, and dissolves readily in organic solvents. It is not hydrolysed by boiling with alcoholic potassium hydroxide, and does not yield benzoyl or acetyl derivatives.

C. H. D.

Action of Phenylhydrazine on Ethyl $\alpha\beta$ -Diacetylpropionate (Ethyl 2:5-Hexadione-3-carboxylate). G. KORSCHUN (*Ber.*, 1904, 37, 2192–2195. Compare Borsche and Spannagel, *Annalen*, 1904, 331, 315).—Phenylhydrazine converts ethyl 2:5-hexadione-3-carboxylate in ethereal solution into the *diphenylhydrazone*,



which crystallises from alcohol and decomposes at 130°.

When only 1 mol. of phenylhydrazine is employed in alcoholic solution, no monophenylhydrazone is obtained, but the diphenylhydrazone is formed together with the ester of an *acid*, $C_{13}H_{14}O_2N_2$, which crystallises from alcohol and melts and decomposes at 210° when rapidly heated. The same acid is produced in larger quantity when phenylhydrazine acetate reacts with the keto-ester.

C. H. D.

Synthesis of Methyl 2:5-Dimethylpyrrole-3-carboxylate. G. KORSCHUN (*Ber.*, 1904, 37, 2196–2197).—*Methyl 2:5-dimethylpyrrole-3-carboxylate*, prepared from methyl acetoacetate, chloroacetone, and dilute ammonia in the manner employed by Hantzsch (*Abstr.*, 1890, 1155) for the preparation of the ethyl ester, crystallises from dilute alcohol and melts at 119.5° and boils at 170° under 15 mm. pressure.

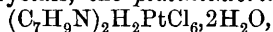
The reaction was explained by Hantzsch as being due to the intermediate formation of ethyl β -aminocrotonate. It is not, however, possible to prepare the ester directly from ethyl β -aminocrotonate and chloroacetone, and the reaction is better explained by the formation of an ester of diacetopropionic acid, which then condenses with ammonia to form the pyrrole derivative.

C. H. D.

Pyridine Bases in Brown-coal Tar. KREY (*Zeit. angew. Chem.*, 1904, 17, 624).—The author proved, in 1887, that pyridine bases occur in brown-coal tar.

A. McK.

Bases from Coal Tar. FELIX B. AHRENS and RICHARD GORKOW (*Ber.*, 1904, 37, 2062–2066. Compare *Abstr.*, 1895, i, 390; 1897, i, 203; 1903, i, 515).—2:5-Dimethylpyridine has been isolated from a fraction of coal tar boiling at 160–165° by means of its *mercurichloride* derivative, $C_7H_9N \cdot HCl \cdot 6HgCl_2$, which melts at 162–164°. The base distils at 159–160° (corr.); the *aurichloride* forms golden-yellow crystals, the *platinichloride*,



brick-red crystals melting at 192–194°, and the *picrate* yellow needles melting at 156–157°. On oxidation with 2 per cent. permanganate

it yields an acid melting at 244° and giving a red coloration with ferrous sulphate solution. When this acid is heated at 250° , it loses carbon dioxide and yields isocinchomeronic acid. 2:5-Dimethylpiperidine, purified by the acid of its nitrosoamine, forms a clear liquid, distilling at $138-140^{\circ}$ (corr.). The *hydrochloride* crystallises in well-developed needles melting at $194-195^{\circ}$. The *hydrobromide* melts at $148-149^{\circ}$, the *hydriodide* at $167-168^{\circ}$, the *platinichloride* at 210° , and the *aurichloride* at about 80° .

A fraction of coal tar boiling at $165-170^{\circ}$ gave a *mercurichloride* melting at $172-173^{\circ}$, which, on decomposition with potassium hydroxide, gave 3:5-dimethylpyridine, boiling at 171° (corr.). The *platinichloride* crystallises in quadratic plates melting at $254-255^{\circ}$, the *aurichloride* melts at $146-147^{\circ}$, and the *picrate* at $228-230^{\circ}$. The base on oxidation yields pyridine-2:4-dicarboxylic acid.

2:4-Dimethylpyridine yields a *hydrochloride*, which is hygroscopic and melts at $195-197^{\circ}$. The *hydrobromide* melts at $189-190^{\circ}$ and the *aurichloride* at 75° .

1-Amino-2:4-dimethylpiperidine, $C_5H_8Me_2N \cdot NH_2$, obtained by the electrolytic reduction of a 50 per cent. sulphuric acid solution of nitroso-2:4-dimethylpiperidine, is a liquid distilling at $170-175^{\circ}$.

J. J. S.

Derivatives of 2-Picolyl- and 2-Picolylmethyl-alkines. II. Coniceines. KARL LÖFFLER (*Ber.*, 1904, 37, 1879-1899. Compare this vol., i, 265).—The constitution of the four isomeric coniceines obtained by Hofmann (*Abstr.*, 1885, 401) and Lellmann (*Abstr.*, 1890, 1328) has not yet been determined. Their relation to 2-pipecolylmethylalkines has been shown by Ladenburg (*Abstr.*, 1890, 67).

Fuming hydrobromic acid and red phosphorus at 125° convert 2 pipecolylalkine into a *bromide*, $C_7H_{14}NBr$, which decomposes on distillation. The *hydrochloride*, $C_5NH_{10} \cdot C_2H_4Br, HCl$, forms small, hygroscopic needles and melts at 148° . The iodo-base is prepared in similar manner and forms a *hydriodide*, $C_7H_{14}NI, HI$, melting at $162-163^{\circ}$, which by moist silver chloride is converted into the *hydrochloride* of the chloro-base, sintering at 148° and melting at 149.5° . The *aurichloride*, $C_7H_{14}NCl, HAuCl_4$, forms microscopic crystals and melts at 110.5° . Bases resembling coniceine could not be prepared by heating the salts with sodium hydroxide.

Hydriodic acid and red phosphorus at 140° convert 2-pipecolylmethylalkine (Ladenburg, *Abstr.*, 1898, i, 687) into a mixture of two oily bases, the *hydriodides* of which melt at 161° and 163° respectively. When heated with concentrated sodium hydroxide in a sealed tube at 100° , volatile bases are produced.

Base I, from the hydriodide melting at 163° , is a colourless, volatile liquid, fuming strongly with hydrogen chloride. It has the properties of a saturated tertiary base, $C_8H_{15}N$. Its boiling point and the properties of its salts agree with those of ϵ -coniceine, prepared by Hofmann and Lellman from iodoconine (*loc. cit.*). The *methiodide* forms a white powder and melts at $185-186^{\circ}$, the *ethiodide* forms colourless crystals and melts at $176-177^{\circ}$; its solution in

hydrochloric acid forms a *platinichloride*, $(C_8H_{15}N, EtCl)_2PtCl_4$, crystallising in needles and melting and decomposing at $198-200^\circ$.

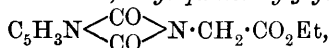
The base II, $C_8H_{15}N$, from the hydriodide melting at 161° , boils at $158-161^\circ$, but was not obtained in sufficient quantity for complete characterisation. The aurichloride melts at $183-184^\circ$, and the picrate melts and decomposes at 222° . It is probably the inactive form of α -coniceine, and identical with the coniceine obtained by the action of fuming hydrochloric acid on pipecolylmethylalkine, with which it corresponds in all the properties examined.

Active α -coniceine, prepared by the action of fuming hydrochloric acid on conhydrine, has $[\alpha]_D + 18.4^\circ$. The *mercurichloride*,

$C_8H_{15}N, HCl, 6HgCl_2$, melts and decomposes at $220-221^\circ$; the *ethiodide* melts at $170-171^\circ$ and forms the chloride with moist silver chloride. The *platinichloride* of the ethyl chloride, $(C_8H_{15}N, EtCl)_2PtCl_4$, decomposes at $208-210^\circ$.

The inactive form, prepared from pipecolylmethylalkine, forms similar salts and must have the constitution $\begin{array}{c} CH_2 \cdot CH_2 \cdot CH \cdot CH_2 \\ | \quad \quad | \\ CH_2 \cdot CH_2 \cdot N \cdot CHMe \end{array}$, being stereoisomeric with the coniceine prepared from pipecolylmethylalkine iodide.
C. H. D.

Derivatives of Quinolinic Acid. BRUNO FELS (*Ber.*, 1904, 37, 2129—2137).—The *potassium* derivative of the imide of quinolinic acid, $C_5H_3N \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} NK$, prepared by bringing the imide (Philips, *Abstr.*, 1895, i, 572) and potassium together in alcoholic solution, forms a colourless mass of glistening platelets. When heated with ethyl chloro- or bromo-acetate, *ethyl quinolinylglycinate*,



is formed; this crystallises in glistening, cream-coloured plates, sinters at 120° , and melts at 122° . *Methyl dihydroxyquinopyrpyne carboxylate*,

$C_5H_3N \begin{smallmatrix} \diagup CO \cdot NH \\ \diagdown CO \cdot CH \cdot CO_2Me \end{smallmatrix}$, is prepared from the foregoing compound on

heating it with sodium methoxide; it crystallises in long, flat, silver-grey needles, and on heating becomes coloured at 180° , strongly so at 200° , and melts and decomposes at $203-205^\circ$. On boiling with hydrogen iodide,

dioxyquinopyrpyne, $C_5H_3N \begin{smallmatrix} \diagup CO \cdot NH \\ \diagdown CO \cdot CH_2 \end{smallmatrix}$, is formed, crystallising in

yellow needles, which, on heating, become brown at 225° and still darker at 245° without melting. The base is easily soluble in dilute acids and alkali hydroxides, giving pale to brownish-yellow solutions; the *hydrochloride* forms chrome-yellow needles, the *hydriodide* glistening, bright orange prisms, the *aurichloride* reddish-yellow bunches of needles, the *platinichloride* characteristic mahogany-brown crystals shaped like an ear of corn; whilst the *picrate* crystallises in flat, lustrous, golden-yellow needles, which sinter at 202° and melt and decompose at 205° . Dioxyquinopyrpyne is very easily oxidised by the atmospheric oxygen, and cannot therefore be recrystallised from water; on oxidation with hydrogen peroxide in aqueous ammonia, a

substance is formed giving a bright red, crystalline hydrochloride the composition of which is not yet satisfactorily determined.

E. F. A.

Derivatives of Cinchomeronic Acid. BRUNO FELS (*Ber.*, 1904, 37, 2137—2149).—*Benzylidenemeride*, $C_5NH_3 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}(\text{CHPh}) \end{smallmatrix} \text{O}$, produced by condensing cinchomeronic anhydride with phenylacetic acid, forms colourless, stellate crystals melting at 178—180°; by the action of sodium methoxide, it is converted into 1:3-diketo-2-phenylhydro-6-pyridin, $C_5H_3N \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{CHPh}$, which crystallises in dark bluish-violet needles and forms a brilliant red-coloured *hydrochloride*. The *barium* derivative, and the *silver* derivative crystallise in carmine-red needles. 4-Phenylacetylpyridine-3-carboxylic acid, $CH_2Ph \cdot CO \cdot C_5NH_3 \cdot CO_2H$, is produced on warming benzylidenemeride with strong alkali hydroxide, and crystallises in well-formed, colourless, rhombic plates melting at 187—188°; the citron-yellow prisms of the *hydrochloride* melt and decompose at 225—260°. The corresponding *amide*, which is formed on heating benzylidenemeride with alcoholic ammonia under pressure, crystallises in colourless, glistening prisms which sinter at 203° and melt at 205—206°.

Benzylidenemerimidine, $C_5NH_3 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}(\text{CHPh}) \end{smallmatrix} NH$, crystallises from chloroform in colourless plates, melting at 234—236°. On reducing it with hydrogen iodide and phosphorus, 4-phenylethylpyridine-3-carboxylic acid, $CH_2Ph \cdot CH_2 \cdot C_5NH_3 \cdot CO_2H$, is formed; this melts at 156—157° and forms a *picrate* crystallising in canary-yellow needles, which sinter at 154° and melt at 166—167°. On dry distillation with lime, 4-phenylethylpyridine is formed; this melts at 69—71° and gives a *platinichloride* melting and decomposing at 214—215°, a *picrate* melting at 162—163°, and an *aurichloride* melting at 183—185° when heated quickly. On oxidation with permanganate, *isonicotinic acid* is formed.

E. F. A.

Behaviour of 2-Methyltetrahydroisoquinoline towards Chromic Acid. MARTIN FREUND and HEINRICH BECK (*Ber.*, 1904, 37, 1942—1946. Compare Beckett and Wright, *Trans.*, 1876, 23, 577, and Freund and Will, *Abstr.*, 1887, 1057).—Unlike hydrocotarnine and hydrohydrastinine, which yield cotarnine and hydrastinine respectively, the nearly-related 2-methyltetrahydroisoquinoline (Wedekind and Oechslen, *Abstr.*, 1902, i, 118) does not yield an aldehydic product on oxidation with chromic acid, but forms 1:3:4-triketo-2-methyltetrahydroisoquinoline, $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{NMe} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{CO} \end{smallmatrix}$, crystallising from alcohol in yellow needles and melting at 186—187°. The *mono-oxime*, $C_{10}H_8O_3N_2$, melts at 207—208°.

Potassium permanganate oxidises the triketone in alkaline solution to the *methylimide* of phthalic acid, $C_9H_7O_2N$, melting at 133—134°

and dissolving sparingly in water. The same compound was prepared by heating methylamine phthalate.

Concentrated potassium hydroxide decomposes the triketone on boiling, methylamine being evolved. The residue contains a compound, $C_{15}H_{12}O_7$, which crystallises from hot water and melts at 199° , and forms crystalline barium and silver salts. C. H. D.

*iso*Carbostyryl Derivatives containing a Meta-substituted Benzene Nucleus. HERRMANN KUSEL (*Ber.*, 1904, 37, 1971—1979).—

4-Ethoxyphthalylglycine, $OEt \cdot C_6H_3 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} N \cdot CH_2 \cdot CO_2H$, prepared by heating 4-ethoxyphthalic anhydride with glycine at 140° , crystallises from water in flat needles and melts at 179° ; the ethyl ester,

$OEt \cdot C_6H_3 : (CO)_2 : N \cdot CH_2 \cdot CO_2Et$, crystallises from alcohol in large, colourless needles, melts at 118° , and, on being heated with alcoholic sodium ethoxide for 3 hours at 100° , gives ethyl 4-hydroxy-6-(or 7)-ethoxyisocarbostyryl-3-carboxylate,

$OEt \cdot C_6H_3 \begin{smallmatrix} \diagup CO-NH \\ \diagdown C(OH) : C \cdot CO_2Et \end{smallmatrix}$. This crystallises from alcohol or water

in colourless needles, melts and decomposes at 233° , and, on hydrolysis with hydrobromic or hydriodic acid, gives 1:4:6- or 1:4:7-trihydroxy-

isoquinoline, $OH \cdot C_6H_3 \begin{smallmatrix} \diagup CO-NH \\ \diagdown CO \cdot CH_2 \end{smallmatrix}$ or $OH \cdot C_6H_3 \begin{smallmatrix} \diagup C(OH) : N \\ \diagdown C(OH) : CH \end{smallmatrix}$, which

crystallises from water in needles and does not melt at 300° ; by reduction with hydriodic acid and red phosphorus, 1:6- or 1:7-dihydroxyisoquinoline is obtained. It crystallises from water in colourless needles, melts at 270° , and is converted by phosphorus oxychloride into 1:6- or 1:7-dichloroisoquinoline, which crystallises in slender needles, is volatile with steam, and melts at $95.5-96^\circ$.

4-Ethoxyphthalylglycine ethyl ester is converted by methyl-alcoholic sodium methoxide into methyl 4-hydroxy-6-(or 7)-methoxyisocarbostyryl-3-carboxylate, $C_{12}H_{11}O_5N$, which crystallises from methyl alcohol in colourless needles and melts and decomposes at 248° .

On oxidation of an acid solution of 1:4:6- or 1:4:7-trihydroxyisoquinoline with hydrogen peroxide, a dihydroxycarbindigotin,

$OH \cdot C_6H_3 \begin{smallmatrix} \diagup CO-NH \\ \diagdown CO \end{smallmatrix} C : C \begin{smallmatrix} \diagup NH-CO \\ \diagdown CO \end{smallmatrix} C_6H_3 \cdot OH$, is obtained; it is also

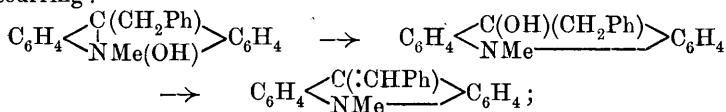
formed, but more slowly, by the atmospheric oxidation of an alkaline solution of the trihydroxyisoquinoline, and by crystallisation from concentrated sulphuric acid is obtained in red needles.

4-Ethoxyphthalylalanine, $OEt \cdot C_6H_3 : (CO)_2 : N \cdot CHMe \cdot CO_2H$, prepared by adding alanine to fused 4-ethoxyphthalic anhydride at $145-150^\circ$, crystallises from water in elongated leaflets and melts at 146° ; the ethyl ester, $C_{15}H_{17}O_5N$, crystallises from alcohol, melts at 78° , and is transformed by alcoholic sodium ethoxide at 100° into 3-methyl-4-hydroxy-6-(or 7)-ethoxyisocarbostyryl, which crystallises from water with $1H_2O$ and decomposes at 285° ; on hydrolysis with concentrated hydriodic acid, the ethoxy-derivative gives 3-methyl-1:4:6- or 1:4:7-trihydroxyisoquinoline, crystallising from water and decomposing at 240° .

W. A. D.

Ammonium Compounds. XVII. Formation of Non-oxygenated Tertiary Bases from Cyclammonium Hydroxides. HERMAN DECKER and THEODOR HOCK (*Ber.*, 1904, 37, 1564—1569).—

9-Benzylacridine, $C_6H_4 \begin{smallmatrix} \diagup C(C_7H_7) \\ \diagdown N \end{smallmatrix} C_6H_4$, prepared by heating phenylacetic acid, diphenylamine, and zinc chloride for 20 hours at 180—200°, crystallises in bright yellow, volatile leaflets and melts at 173°; the **picrate**, $C_{26}H_{18}O_7N_4$, forms yellow crystals and melts at 230°. The **methiodide**, $C_6H_4 \begin{smallmatrix} \diagup C(C_7H_7) \\ \diagdown NMeI \end{smallmatrix} C_6H_4$, prepared by the direct addition of methyl iodide at 100°, crystallises in small, dark red cubes; the analogous **9-benzylacridinium 10-methopicrate**, $C_{27}H_{20}O_7N_4$, prepared by precipitating the methiodide with alcoholic picric acid, melts at 189°. On decomposing the quaternary salts with sodium hydroxide, **9-benzylidene-10-methyl-9:10-dihydroacridine**, $C_6H_4 \begin{smallmatrix} \diagup C(CHPh) \\ \diagdown NMe \end{smallmatrix} C_6H_4$, is obtained, probably owing to the following series of changes occurring:



the product crystallises from benzene or light petroleum in large, bright yellow cubes, melts at 141°, and combines with picric acid to form the foregoing 9-benzylacridinium 10-methopicrate. It is slowly oxidised in the air giving benzaldehyde and 10-methyl-9-acridone, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown NMe \end{smallmatrix} C_6H_4$.

The foregoing changes are of importance, principally on account of the light that they throw on the nature of the isopapaverine bases (Decker and Clausen, this vol., i, 338). W. A. D.

Nitroso-*m*-phenylenediamine. K. BERTELS (*Ber.*, 1904, 37, 2276—2282. Compare Täuber and Walder, *Abstr.*, 1900, i, 566).—Nitroso-*m*-phenylenediamine is oxidised by hydrogen peroxide, in presence of ammonia, to nitrophenylenediamine [$NO_2:(NH_2)_2 = 1:2:4$], which melts at 157° (Barbaglia, *Ber.*, 1874, 7, 1257, gives m. p. 161°).

When warmed with aqueous sodium hydroxide, nitroso-*m*-phenylenediamine evolves ammonia and forms 4-nitroso-3-aminophenol, which crystallises in long, red needles, melts and decomposes at about 200°, loses ammonia when acted on by concentrated aqueous alkali hydroxides, and is reduced by stannous chloride in hydrochloric acid solution to 3:4-diaminophenol. Contrary to Köhler's statement (*Abstr.*, 1884, 1159), the hydrochloride of 3:4-diaminophenol is not soluble in concentrated hydrochloric acid.

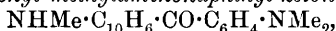
m-Phenylenediamine condenses with benzaldehyde to form a triphenylmethane derivative, which gives a strong, yellow fluorescence when heated with hydrochloric acid at 160—170°. Nitroso-*m*-phenylenediamine, when warmed with benzaldehyde, forms a dibenzylidene derivative, which melts and decomposes at 240°. When

nitroso-*m*-phenylenediamine is heated with benzylidene chloride, or with benzaldehyde and hydrochloric acid, or when the dibenzylidene derivative is boiled with dilute hydrochloric acid, a *benziminazole* compound, $C_{13}H_{11}ON_3$, is formed. This crystallises in delicate, yellow needles, melts at 164° , and forms red dyes when diazotised and coupled with β -naphthol or naphthionic acid. With benzaldehyde, 4-nitroso-3-aminophenol condenses in a similar manner; the *product* contains H_2O . G. Y.

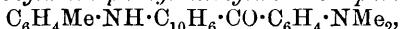
Dyes of the Diphenylnaphthylmethane, Phenyldinaphthylmethane, and Trinaphthylmethane Series. EMILIO NOELTING [and, in part, GEORG FREYSS, SERRA, DREYFUS, BOURRY, and JULES DEMANT] (*Ber.*, 1904, 37, 1899—1920).—Derivatives of diphenylnaphthylmethane have been studied by Nathanson and Müller (*Abstr.*, 1889, 1188), and derivatives of phenyldinaphthylmethane by Friedländer and Wellmanns (*Abstr.*, 1889, 150); trinaphthylmethane compounds have not hitherto been described.

Diaminophenylnaphthyl ketones may be prepared by condensing dimethyl-*p*-aminobenzomethylanilide with alkylated α -naphthylamines by means of phosphorus oxychloride. The red aurammonium chlorides thus obtained are decomposed by alcohol and sodium hydroxide, yielding the ketones.

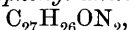
Dimethylaminophenyl methylaminonaphthyl ketone,



forms bright yellow crystals and melts at 211 — 212° . *Dimethylaminophenyl ethylaminonaphthyl ketone*, $C_{21}H_{22}ON_2$, forms green, prismatic crystals and melts at 162° ; *dimethylaminophenyl anilinonaphthyl ketone*, $C_{25}H_{22}ON_2$, forms bright yellow needles and melts at 201 — 202° ; *dimethylaminophenyl methylanilinonaphthyl ketone,*



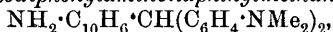
forms bright yellow needles and melts at 221° ; *diethylaminophenyl methylaminonaphthyl ketone*, $C_{22}H_{24}ON_2$, forms large, yellow crystals and melts at 149° ; the *ethyl* compound forms green or yellow crystals and melts at 133.5° ; *diethylaminophenyl anilinonaphthyl ketone,*



forms thick, yellow crystals and melts at 146 — 147° ; *diethylaminophenyl methylanilinonaphthyl ketone*, $C_{28}H_{28}ON_2$, forms greenish-yellow needles and melts at 176 — 177° .

The ketones are weak bases, dissolving in concentrated acids, but being reprecipitated on dilution. Sodium amalgam reduces their alcoholic solutions, forming the corresponding hydrols. Fusion with zinc chloride and ammonium chloride converts them into auramines. The *auramine* $NH_2Et \cdot C_{10}H_6 \cdot C(NH) \cdot C_6H_4 \cdot NMe_2$ forms large, slightly yellow prisms and melts at 199 — 200° , its *hydrochloride* forms red prisms. The *auramine* $NHPh \cdot C_{10}H_6 \cdot C(NH) \cdot C_6H_4 \cdot NMe_2$ melts at 186° and the *auramine* $C_7H_7 \cdot NH \cdot C_{10}H_6 \cdot C(NH) \cdot C_6H_4 \cdot NMe_2$ at 164 — 165° .

Tetramethyldiaminodiphenylaminonaphthylmethane,

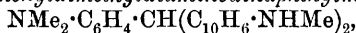


forms glistening leaflets and melts at 221 — 222° ; its *acetyl* derivative forms colourless crystals and melts at 228 — 229° . The *methylamino-*

naphthyl compound melts at 201—202°, the corresponding *ethyl* derivative at 172—173°, the *phenyl* derivative at 167—168° (compare Nathanson and Müller, *loc. cit.*), and the *p-tolyl* derivative at 193—194°.

Tetramethyldiaminodiphenyl-diaminonaphthylmethane, from tetramethyldiaminobenzhydrol and *o*-naphthylenediamine, melts at 233—234°, and its *diacetyl* derivative at 258—259°. The base, $C_{41}H_{34}N_4$, obtained by condensing the diaminonaphthyl compound with phenanthraquinone, forms small, yellow needles and melts above 336°.

Dimethylaminophenyldimethyldiaminodinaphthylmethane,



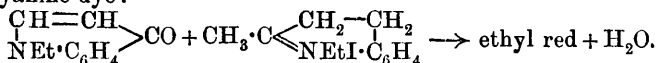
forms a yellow, amorphous powder, without definite melting point; the *diethyl* derivative forms thick, colourless prisms and melts at 220°; the *diphenyl* and *di-p-tolyl* derivatives form white, amorphous powders without definite melting point.

Nitrodimethylaminophenyldimethyldiaminodinaphthylmethane, from 3-nitro-4-dimethylaminobenzaldehyde and methyl- α -naphthylamine, forms an amorphous powder, the *diethyl* derivative forms red prisms, and melts at 200°; the *diphenyl* and *di-p-tolyl* derivatives are yellow, amorphous powders without definite melting point.

Triethyltriaminotrinenaphthylmethane, from ethyl orthoformate and ethyl- α -naphthylamine, forms colourless, glistening needles and melts above 300°.

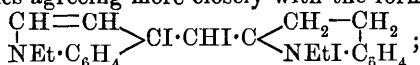
The colouring matters obtained by the oxidation of these leucobases, or by direct condensation, are also described and tabulated. They form blue, or greenish-blue crystals with metallic lustre, the shade becoming greener as the number of naphthyl groups is increased. C. H. D.

Constitution of the Cyanine Dyes. A. MIETHE and GILBERT BOOK (*Ber.*, 1904, 37, 2008—2022).—On adding potassium hydroxide to an alcoholic solution of quinoline ethiodide, a dye of the cyanine series is not obtained, showing that the presence of a methyl group, such as exists in quinaldine or lepidine, is necessary for the condensation; quinaldine ethiodide, on the other hand, is readily converted into a dye by alcoholic alkali. Ethyl-red (diethylisocyanine), which is obtained by the action of potassium hydroxide on a mixture of quinoline and quinaldine ethiodides in various proportions, best when the quinoline and quinaldine are in the molecular ratio 2:1, is considered to have the structure
$$\begin{array}{c} CH=CH \\ | \quad | \\ NEt \cdot C_6H_4 \end{array} > C:CH \cdot C \begin{array}{c} \diagup CH_2-CH_2 \\ \diagdown NEtI \cdot C_6H_4 \end{array}.$$
 The quinoline ethiodide is first probably converted into α -quinolone, thus:
$$C_6H_4 \begin{array}{c} \diagup NEtI:CH \\ \diagdown CH=CH \end{array} \rightarrow C_6H_4 \begin{array}{c} \diagup NEt(OH):CH \\ \diagdown CH=CH \end{array} \rightarrow C_6H_4 \begin{array}{c} \diagup NEt \cdot CH \\ \diagdown CO-CH \end{array} + H_2;$$
 the hydrogen formed reduces quinaldine ethiodide to a hydro-quinaldine ethiodide, which then condenses with α -quinolone, giving the cyanine dye:



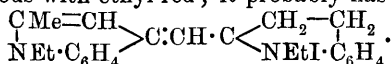
The new formula explains the fact that the additive product formed

by ethyl-red with iodine is not a periodide, like quinoline periodide, but has properties agreeing more closely with the formula



thus it does not impart a blue colour to starch paste even in presence of acid, and is decolorised by hydrochloric acid, whereas quinoline periodide at once turns starch blue and does not lose its colour in presence of dilute hydrochloric acid.

When 3 mols. of quinaldine ethiodide are heated with two mols. of alcoholic potassium hydroxide, a cyanine dye, $\text{C}_{24}\text{H}_{27}\text{N}_2\text{I}$, is produced, which is homologous with ethyl-red; it probably has the structure



It is much less valuable as a sensitiser of gelatin bromide plates than ethyl-red, as is shown by the curves of induced sensibility which are given for the two substances.

Silver nitrate converts ethyl-red into a *nitrate*, $\text{C}_{23}\text{H}_{25}\text{N}_2(\text{NO}_3)$, which crystallises in large, dark green prisms and is formed by a replacement of the iodine atom by the radicle NO_3 . W. A. D.

Ethyl Benzoylpyruvate and its Derivatives. CARL BÜLOW (*Ber.*, 1904, 37, 2198—2209. Compare *Abstr.*, 1903, i, 647).—Ethyl benzoylpyruvate reacts with methylamine to form dimethoxamide, $\text{C}_2\text{O}_2(\text{NHMe})_2$, acetophenone, and alcohol.

Hydrazine and ethyl benzoylpyruvate in glacial acetic acid solution yield *ethyl 5-phenylpyrazole-3-carboxylate*, which crystallises from dilute alcohol in large needles, melts at 140° , and dissolves readily in organic solvents. Two mols. of hydrazine in alcoholic solution yield oxalodihydrazide, together with *hydrazine 5-phenylpyrazole-3-carboxylate*, $\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_4$, which crystallises from hot water in glistening, white leaflets, and melts at 203° and decomposes at 255° , the residue again solidifying to a white mass. When boiled with a small quantity of water, the salt dissolves, but rapidly deposits *5-phenylpyrazole-3-carboxylic hydrazide*, $\text{C}_3\text{N}_2\text{H}_2\text{Ph} \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$, melting at 205° .

5-Phenylpyrazole-3-carboxylic acid, prepared by hydrolysis of the ester, melts and decomposes at 231 — 232° (compare Wenglein, *Diss.* Jena, 1895).

Diazobenzene chloride and ethyl benzoylpyruvate form *ethyl benzeneazobenzoylpyruvate*, $\text{COPh} \cdot \text{CH}(\text{N} \cdot \text{NPh}) \cdot \text{CO} \cdot \text{CO}_2\text{Et}$, crystallising from alcohol in yellow needles and melting at 115 — 116° . Phenylhydrazine acetate converts it into *ethyl 1:5-diphenyl-4-benzeneazopyrazole-3-carboxylate*, crystallising in orange leaflets and melting at 148 — 149° .

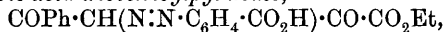
Ethyl 5-phenyl-4-benzeneazoisooxazole-3-carboxylate from ethyl benzeneazobenzoylpyruvate and hydroxylamine forms yellow needles and melts at 99 — 100° . The corresponding *acid*, $\text{C}_{16}\text{H}_{11}\text{O}_3\text{N}_3$, is produced at the same time and melts at 217° . Alcoholic potassium hydroxide decomposes the isooxazole ester, forming *benzeneazobenzoylacetonitrile*, $\text{OH} \cdot \text{CPh} \cdot \text{C}(\text{CN}) \cdot \text{N} \cdot \text{NPh}$, crystallising in yellow needles and melting at 135 — 136° .

Ethyl benzeneazobenzoylpyruvate and hydrazine hydrate form

5-phenyl-4-benzeneazopyrazole-3-carboxylic acid, separating from dilute acetic acid in reddish-brown crystals with golden lustre, and melting and decomposing at 247—248°, together with the *ethyl ester* melting at 153°.

Sodium benzoylpyruvate and diazobenzene chloride form *benzeneazobenzoylpyruvic acid*, crystallising from dilute alcohol in slender, yellow needles and decomposing at 140—150°.

Ethyl o-benzoic-acid-azobenzoylpyruvate,



from ethyl benzoylpyruvate and diazotised anthranilic acid, crystallises from dilute acetic acid in yellow needles and melts and decomposes at 158—160°. The *disazo*-compound from benzidine forms a brown, crystalline powder. C. H. D.

5-Chloro-1-*o*-tolyl-3-methylpyrazole and 1-Phenyl-3-methyl-5-pyrazolone-2'-carboxylic Acid. AUGUST MICHAELIS and C. EISENSCHMIDT (*Ber.*, 1904, 37, 2228—2231. Compare Abstr., 1900, i, 696).—When heated with phosphorus oxychloride for 10 hours at 150°, Knorr's *o*-tolylmethylpyrazolone yields 5-chloro-1-*o*-tolyl-3-methylpyrazole, which crystallises from alcohol in colourless crystals melting at 56°. It turns red on exposure to the air, and is soluble in concentrated hydrochloric acid. The *methiodide*, $\text{C}_{12}\text{H}_{14}\text{N}_2\text{ClI}$, crystallises in colourless plates melting at 231—232°; the *methochloride* crystallises from water with $2\text{H}_2\text{O}$, which it loses at 112°, and then melts at 210°; its *picrate*, $\text{C}_{12}\text{H}_{14}\text{N}_2\text{Cl} \cdot \text{O} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3$, forms a yellow precipitate.

On oxidation, the *o*-tolylpyrazole derivative yields 5-chloro-1-phenyl-3-methylpyrazole-2'-carboxylic acid, $\begin{array}{c} \text{CMe}=\text{N} \\ | \\ \text{CH}:\text{CCl} \end{array} > \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, which crystallises from dilute acetic acid in colourless needles melting at 169° and is insoluble in water. The *barium* salt containing $3\text{H}_2\text{O}$, *calcium* salt which is anhydrous, and the *ethyl ester*, a colourless oil distilling at 315°, have been prepared.

When heated, the chloro-acid loses hydrogen chloride, yielding the *anhydride*, $\text{CMe} < \begin{array}{c} \text{N}-\text{N} \cdot \text{C}_6\text{H}_4 \\ | \quad | \\ \text{CH}:\text{C} \quad \text{O} \end{array} > \text{CO}$, which melts at 109° and boils at 345°. The anhydride combines with water forming 1-phenyl-3-methylpyrazolone-2'-carboxylic acid melting at 139°. J. J. S.

Pyrimidine Derivatives. 5-Methylcytosine. HENRY L. WHEELER and TREAT B. JOHNSON (*Amer. Chem. J.*, 1904, 31, 591—606. Compare Abstr., 1903, i, 524, 526).—2-Ethylthiol-5-methyl-6-oxypyrimidine, $\text{NH} < \begin{array}{c} \text{C}(\text{SEt})\text{:N} \\ | \quad | \\ \text{CO} \quad \text{CMe} \end{array} > \text{CH}$, obtained by the action of ψ -ethylthiocarbamide hydrobromide on ethyl sodioformylpropionate, crystallises from hot water in long, slender prisms, melts at 158—159°, and is very soluble in alcohol. When this compound is warmed with phosphorus pentachloride, it is converted into 6-chloro-2-ethylthiol-5-methylpyrimidine, $\text{N} < \begin{array}{c} \text{C}(\text{SEt})\text{:N} \\ | \quad | \\ \text{CCl} \quad \text{CMe} \end{array} > \text{CH}$, which forms a colourless, oily

liquid and boils at 146—147° under 17 mm. and at 157—159° under 25—26 mm. pressure. 6-Chloro-2-ethylthiopyrimidine boils at 135° under 24 mm. pressure. 6-Amino-2-ethylthiol-5-methylpyrimidine, $N \begin{smallmatrix} \text{C(SEt)} \\ \text{C(NH}_2\text{)} \end{smallmatrix} \begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \text{N} \begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \text{CH} \cdot \text{CMe}$, obtained by heating 6-chloro-2-ethylthiol-5-methylpyrimidine with alcoholic ammonia, crystallises in colourless prisms, melts at 96—97°, and is readily soluble in alcohol and sparingly so in water. By the action of alcoholic ammonia on 6-chloro-2-ethylthiopyrimidine, 6-ethoxy-2-ethylthiopyrimidine, $N \begin{smallmatrix} \text{C(SEt)} \\ \text{C(OEt)} \end{smallmatrix} \begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \text{N} \begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \text{CH} \cdot \text{CMe}$, is produced, which boils at 137—138° under 18 mm. pressure, and, when heated with concentrated hydrochloric acid, is converted quantitatively into uracil.

When 6-amino-2-ethylthiopyrimidine is heated with concentrated hydrochloric acid for 3—4 hours on the water-bath, 6-amino-2-oxypyrimidine (cytosine) *dihydrochloride* is obtained which crystallises in flat, colourless prisms. If 6-amino-2-ethylthiol-5-methylpyrimidine is treated in a similar manner, 6-amino-5-methyl-2-oxypyrimidine *hydrochloride* is produced, which melts and decomposes at 288°; a basic *hydrochloride* and a basic *hydrobromide* are also described. 6-Amino-5-methyl-2-oxypyrimidine (5-methylcytosine), $N \begin{smallmatrix} \text{CO} \\ \text{C(NH}_2\text{)} \end{smallmatrix} \begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \text{NH} \begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \text{CH} \cdot \text{CMe}$, forms colourless, prismatic crystals containing $\frac{1}{2} \text{H}_2\text{O}$, melts and decomposes at 270°, is soluble in water at 25° to the extent of 4.5 per cent., and yields a white precipitate with phosphotungstic acid; its *acetyl* derivative crystallises in needles and decomposes between 255° and 290°; the *picrate* and *platinichloride* are also described.

5-Bromo-2-ethylthiol-6-oxypyrimidine, $NH \begin{smallmatrix} \text{C(SEt)} \\ \text{CO} \end{smallmatrix} \begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \text{N} \begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \text{CH} \cdot \text{CBr}$, obtained by the action of bromine on 2-ethylthiol-6-oxypyrimidine, crystallises in colourless, acicular prisms, melts at 189°, is soluble in alcohol and sparingly so in water, and, when boiled with hydrochloric acid, is converted into 5-bromouracil. When 5-bromo-2-ethylthiol-6-oxypyrimidine is warmed with phosphorus pentachloride, 6-chloro-5-bromo-2-ethylthiopyrimidine, $N \begin{smallmatrix} \text{C(SEt)} \\ \text{CCl} \end{smallmatrix} \begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \text{N} \begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \text{CH} \cdot \text{CBr}$, is produced, which forms colourless plates and melts at about 27°. 5-Bromo-6-amino-2-ethylthiopyrimidine, $N \begin{smallmatrix} \text{C(SEt)} \\ \text{C(NH}_2\text{)} \end{smallmatrix} \begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \text{N} \begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \text{CH} \cdot \text{CBr}$, obtained by the action of alcoholic ammonia on 6-chloro-5-bromo-2-ethylthiopyrimidine, crystallises in colourless prisms, melts at 123—124°, and dissolves readily in alcohol and sparingly in water. When this compound is boiled with strong hydrochloric acid, it is converted into 5-bromo-6-amino-2-oxypyrimidine (5-bromocytosine), $N \begin{smallmatrix} \text{CO} \\ \text{C(NH}_2\text{)} \end{smallmatrix} \begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \text{NH} \begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \text{CH} \cdot \text{CBr}$, which crystallises in acicular prisms and decomposes above 235°. 6-Nitroamino-2-oxypyrimidine (nitrocytosine), $N \begin{smallmatrix} \text{CO} \\ \text{C(NH} \cdot \text{NO}_2\text{)} \end{smallmatrix} \begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \text{NH} \begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \text{CH} \cdot \text{CH}$, prepared by the action of a mixture of nitric and sulphuric acids on anhydrous cytosine, crystallises in minute, colourless needles, darkens at 280°, and decomposes rapidly above 300°. E. G.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. VI. Tolyl and Benzyl Derivatives of Furodiazole [1:2:4-Oxadiazole] and 1:3:4-Thiodiazole. ROBERT STOLLE and HENRY P. STEVENS (*J. pr. Chem.*, 1904, [ii], 69, 366—381. Compare Abstr., 1899, i, 456; 1903, i, 721; this vol., i, 102, 200, 453).—*o*-Toluoylethydrazide, formed by the action of boiling ethyl *o*-toluate on hydrazine hydrate, crystallises in delicate needles, melts at 124°, is easily soluble in alcohol, chloroform, acetone, or glacial acetic acid, and reduces ammoniacal silver solutions in the cold, but Fehling's solution only on warming. *o*-Toluoylethydrazide, $\text{C}_7\text{H}_7\cdot\text{CO}\cdot\text{NH}\cdot\text{N}:\text{CHPh}$,

crystallises in white needles and melts at 164°. *o*-Toluoylethoxybenzylidenehydrazide crystallises in yellow needles and melts at 166°.

s-Di-*o*-toluoylethydrazide, formed by the action of iodine on *o*-toluoylethydrazide in warm alcoholic solution, or along with di-*o*-tolylloxadiazole by the action of ethyl *o*-toluate on *o*-toluoylethydrazide in a sealed tube at 150°, crystallises in delicate, white needles, melts at 216—217°, and is soluble in dilute aqueous sodium hydroxide, alcohol, acetone, and chloroform.

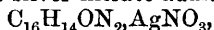
2:5-Di-*o*-tolyl-1:3:4-oxadiazole, $\begin{matrix} \text{N}:\text{C}(\text{C}_7\text{H}_7) \\ | \\ \text{N}:\text{C}(\text{C}_7\text{H}_7) \end{matrix} > \text{O}$, is formed when *s*-di-*o*-toluoylethydrazide is heated at 300°. It distils under reduced pressure, crystallises in white needles, and melts at 121°. It is easily soluble in acetone, chloroform, or petroleum, but only moderately so in ether. It dissolves in concentrated sulphuric acid and is reprecipitated on addition of water. With silver nitrate in alcoholic solution, it forms an additive compound, $\text{C}_{16}\text{H}_{14}\text{ON}_2\cdot 2\text{AgNO}_3$, which crystallises from alcohol, melts at about 156°, and decomposes violently when heated above its melting point.

m-Toluoylethydrazide, prepared in the same way as the *ortho*-compound, crystallises in glistening leaflets and melts at 97°. *m*-Toluoylethoxybenzylidenehydrazide crystallises in needles and melts at 139°. *s*-Di-*m*-toluoylethydrazide is formed by the same reactions as the *ortho*-compound, but no oxadiazole is obtained. It crystallises in clusters of needles and melts at 214—216°.

2:5-Di-*m*-tolyl-1:3:4-oxadiazole is obtained on heating *s*-di-*m*-toluoylethydrazide at 300° and distilling the product under reduced pressure. The distillate is a colourless oil, which crystallises after a time and then melts at 72°. The additive compound with silver nitrate is a white, crystalline powder and melts at 206°.

p-Toluoylethydrazide crystallises in glistening leaflets and melts at 117°; *p*-toluoylethoxybenzylidenehydrazide crystallises in small, white needles and melts at 235°; *p*-toluoylethoxybenzylidenehydrazide crystallises in needles and melts at 197°. *s*-Di-*p*-toluoylethydrazide crystallises in delicate, white needles and melts at 250°. Of the hydrazides, the *ortho*-compounds are the most easily, the *para*- the least easily soluble.

2:5-Di-*p*-tolyl-1:3:4-oxadiazole, formed when *s*-di-*p*-toluoylethydrazide is heated at 300°, crystallises from alcohol in large, colourless needles and melts at 175°. Pinner (Abstr., 1895, i, 138) gives the melting point as 233—234°. The silver nitrate additive compound,



is a crystalline powder which melts at 235°. Pinner (*loc. cit.*) found it to decompose above 280°.

When heated at 300°, *s*-diphenylacetylhydrazide (Boetzelen, Abstr., 1902, i, 58) yields phenylacetoneitrile, which boils at 230—240°, and, with benzaldehyde and alcoholic potassium hydroxide, forms α -phenylcinnamonitrile. 2:5-Dibenzyl-1:3:4-oxadiazole is formed when *s*-diphenylacetylhydrazide is heated at 260—280°, or in better yield when the hydrazide is heated with zinc chloride. It crystallises in yellow needles and melts at 98°. With silver nitrate, it forms a crystalline additive compound which melts at about 120°.

These 1:3:4-oxadiazoles are stable compounds which can be boiled with alkalis or dilute acids without undergoing any change.

2:5-Di-*p*-tolyl-1:3:4-thiodiazole, $\begin{matrix} \text{N}:\text{C}(\text{C}_7\text{H}_7) \\ | \\ \text{N}:\text{C}(\text{C}_7\text{H}_7) \end{matrix} > \text{S}$, is formed when *s*-di-*p*-toluoylhydrazide is heated with phosphorus pentasulphide at 300°. It crystallises in golden plates or short needles, melts at 156—158°, is easily soluble in alcohol, acetone, or chloroform, is precipitated from its solution in concentrated sulphuric acid on addition of water, and resembles the corresponding oxadiazole in its stability.

2:5-Dibenzyl-1:3:4-thiodiazole, prepared by the action of phosphorus pentasulphide on *s*-diphenylacetylhydrazide, crystallises in short, yellow needles and melts at 98°. It is easily soluble in ether, alcohol, acetone, or chloroform, is precipitated on addition of water to its solution in concentrated sulphuric acid, and remains unchanged when boiled with dilute acids or alkalis or when heated with dilute sulphuric acid in a sealed tube at 175°. G. Y.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. VII. Conversion of *s*-Di-*m*-chlorobenzoylhydrazide into Diazole Derivatives. ROBERT STOLLÉ and HANS FOERSTER (*J. pr. Chem.*, 1904, [ii], 69, 382—384. Compare Abstr., 1902, i, 58).—2:5-Di-*m*-chlorophenyl-1:3:4-oxadiazole, $\begin{matrix} \text{N}:\text{C}(\text{C}_6\text{H}_4\text{Cl}) \\ | \\ \text{N}:\text{C}(\text{C}_6\text{H}_4\text{Cl}) \end{matrix} > \text{O}$, is formed when *s*-di-*m*-chlorobenzoylhydrazide is heated with phosphorus pentoxide at 300°. It crystallises in white needles, melts at 144°, and is easily soluble in ether, chloroform, or boiling alcohol. With silver nitrate in alcoholic solution, it forms an additive compound, $\text{C}_{14}\text{H}_8\text{ON}_2\text{Cl}_2 \cdot \text{AgNO}_3$, which crystallises in small, slender needles, melts at 210°, and is moderately sensitive to light.

2:5-Di-*m*-chlorophenyl-1:3:4-thiodiazole, obtained by heating a mixture of *s*-di-*m*-chlorobenzoylhydrazide and phosphorus pentasulphide at 250—300°, crystallises in short, white needles, melts at 151°, and is easily soluble in acetone, chloroform, or concentrated sulphuric acid. From its solution in sulphuric acid, it is precipitated unchanged on addition of water. It is not acted on by boiling dilute acids or alkalis.

2:5-Di-*m*-chlorophenyltriazole, $\begin{matrix} \text{N}:\text{C}(\text{C}_6\text{H}_4\text{Cl}) \\ | \\ \text{N}:\text{C}(\text{C}_6\text{H}_4\text{Cl}) \end{matrix} > \text{NH}$, prepared by heating *s*-di-*m*-chlorobenzoylhydrazide with zinc ammonio-chloride at 300°, crystallises from benzene and melts at 220°. G. Y.

Isomerism in the Amidine Series : Diphenylbenzenylaminoamidine and Phenylbenzenylphenylaminoamidine. HENRY L. WHEELER and TREAT B. JOHNSON (*Amer. Chem. J.*, 1904, 31, 577—584. Compare Abstr., 1903, i, 693).—The statements of Acree (Abstr., 1902, i, 242; 1903, i, 867) with regard to the possibility of desmotropism in the amidine series are discussed, and it is maintained that no evidence of such isomerism in this class of compounds has yet been discovered.

When diphenylbenzenylaminoamidine, the more fusible amidine described by Pechmann (Abstr., 1896, i, 31), is treated with nitrous acid, diphenylbenzenylamidine is produced. The *benzoyl* derivative of diphenylbenzenylaminoamidine crystallises in colourless, rhombic plates and melts at 136°. When the less fusible amidine is treated with benzoic anhydride, no benzoyl derivative is obtained.

By the action of carbonyl chloride on phenylbenzenylphenylaminoamidine (Pechmann's less fusible amidine), 1:3:4-triphenyl-1:2:4-triazolone is obtained, melting at 217—218°. The more fusible amidine combines readily with phenylthiocarbimide with formation of a cream-coloured powder which does not melt below 345° and is sparingly soluble in benzene or alcohol. The less fusible amidine also unites with phenylthiocarbimide with production of a compound which crystallises in needles, melts at about 186°, and is slightly soluble in alcohol. E. G.

Action of Cyanogen Bromide on Hydroxylamine. HEINRICH WIELAND (*Ber.*, 1904, 37, 1536—1542).—All attempts to prepare cyanohydroxylamine by the interaction of cyanogen bromide and hydroxylamine were fruitless; even at -15° the action between the two substances could not easily be regulated. Cyanogen bromide, however, in ethereal solution converts phenylhydroxylamine into the *hydrobromide* of *diphenyldihydroxyguanidine*, $\text{NH}\cdot\text{C}(\text{NPh}\cdot\text{OH})_2$; the *base* forms colourless, felted needles, and cannot be recrystallised without decomposing. It melts and decomposes at 135° , and is easily reduced by stannous chloride and hydrochloric acid to diphenylguanidine.

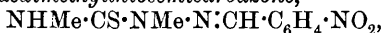
Cyanophenylhydroxylamine, $\text{OH}\cdot\text{NPh}\cdot\text{CN}$, is obtained when cyanogen bromide and sodium hydrogen carbonate are added alternately to an alcoholic solution of phenylhydroxylamine cooled with ice; it crystallises from light petroleum (b. p. 50°) in dazzling, white spangles, melts and decomposes at 60° , and soon decomposes on keeping. The *dihydrochloride*, $\text{C}_7\text{H}_8\text{N}_2\text{OCl}_2$, which melts at 158° , is more stable.

W. A. D.

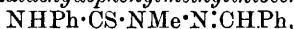
Addition of Alkylcarbimides and Thiocarbimides to Primary Hydrazines. MAX BUSCH, ERICH OPFERMANN, and H. WALTHER (*Ber.*, 1904, 37, 2318—2333).—Busch and Holzmann (Abstr., 1901, i, 234) have shown that the isomerism discovered by Marckwald (Abstr., 1893, i, 46) with thiosemicarbazides is due to the transference of the thiocarbimide grouping from the α - to the β -nitrogen atom of the hydrazine during the conversion of the labile into the stable thiosemi

carbazine. The addition of thiocarbimides to primary aliphyl hydrazines has now been examined, and it is found that methyl- and benzylhydrazines add on thiocarbimides at the α -nitrogen atom; the addition at this particular point in the molecule is not conditioned by temperature, and the $\beta\delta$ -compounds obtained do not, as a rule, suffer transformation into the $\alpha\delta$ -isomerides. The same regularity obtains when alkylcarbimides are substituted for thiocarbimides.

The compound described by Marckwald and Sedlacek as dimethylthiosemicarbazide was prepared by the methods used by these authors and shown to be $\beta\delta$ -dimethylthiosemicarbazide, $\text{NHMe}\cdot\text{CS}\cdot\text{NMe}\cdot\text{NH}_2$. *m*-Nitrobenzaldehydedimethylthiosemicarbazone,



crystallises in glistening, yellow needles and melts at $227-228^\circ$. Methylhydrazine and allylthiocarbimide unite to form β -methyl- δ -allylthiosemicarbazide, $\text{C}_3\text{H}_5\cdot\text{NH}\cdot\text{CS}\cdot\text{NMe}\cdot\text{NH}_2$, which crystallises in transparent plates and melts at 57° ; it does not suffer rearrangement into the isomeric $\alpha\delta$ -compound; it condenses with *m*-nitrobenzaldehyde to form *m*-nitrobenzaldehydemethylallylthiosemicarbazone, which crystallises from alcohol in yellow needles and melts at 132° . β -Methyl- δ -phenylthiosemicarbazide, $\text{NHPh}\cdot\text{CS}\cdot\text{NMe}\cdot\text{NH}_2$, had previously been prepared by Marckwald and Sedlacek, and had been classified by them as a labile (anti-) thiosemicarbazide; it readily condenses with benzaldehyde to form benzaldehydphenylmethylthiosemicarbazone,



which melts at 132° . Phenylmethylthiosemicarbazide methyl ether is a yellow oil, which combines with benzenesulphonic chloride to form the sulphone, which crystallises in white needles melting at $93-94^\circ$. Further proof of the constitution of the methyl ether is afforded by its behaviour towards carbon disulphide, with which it forms dithiocarbazinic acid, $\text{SMe}\cdot\text{NPh}\cdot\text{NMe}\cdot\text{NH}\cdot\text{CS}\cdot\text{SH}$. The methyl ether readily condenses with benzaldehyde to form benzaldehydphenylmethylsemicarbazide, $\text{NHPh}\cdot\text{CO}\cdot\text{NMe}\cdot\text{N}\cdot\text{CHPh}$, which forms white needles melting at 108° ; methyl mercaptan is also produced in the reaction.

β -Methyl- δ -ethylsemicarbazide, $\text{NHEt}\cdot\text{CO}\cdot\text{NMe}\cdot\text{NH}_2$, prepared from methylhydrazine and ethylcarbimide, separates from alcohol in needles, melts at $154-155^\circ$, and reduces Fehling's solution. *m*-Nitrobenzaldehydemethylethylsemicarbazone forms yellow needles and melts at $142-143^\circ$.

δ -Phenyl- β -methylsemicarbazide, $\text{NHPh}\cdot\text{CO}\cdot\text{NMe}\cdot\text{NH}_2$, formed from methylhydrazine and phenylcarbimide, melts at $93-94^\circ$. Benzaldehydphenylmethylsemicarbazone separates from alcohol in slender needles and melts at 108° .

Benzaldehydebenzylsemicarbazone melts at $153-154^\circ$.

β -Benzyl- δ -ethylsemicarbazide, $\text{CH}_2\text{Ph}\cdot\text{N}(\text{CO}\cdot\text{NHEt})\cdot\text{NH}_2$, prepared from benzylhydrazine and ethylcarbimide, condenses with *m*-nitrobenzaldehyde to form *m*-nitrobenzaldehydebenzylethylsemicarbazone, which crystallises in yellow plates, melting at 106° .

δ -Phenyl- β -benzylsemicarbazide, $\text{CH}_2\text{Ph}\cdot\text{N}(\text{CO}\cdot\text{NHPh})\cdot\text{NH}_2$, prepared from benzylhydrazine and phenylcarbimide, separates from alcohol in glassy crystals and melts at $109-110^\circ$; when warmed, it reduces Fehling's solution. Benzaldehydphenylbenzylsemicarbazone melts at 152° .

β -Benzyl- δ -methylthiosemicarbazide, $\text{CH}_2\text{Ph}\cdot\text{N}(\text{CS}\cdot\text{NHMe})\cdot\text{NH}_2$, prepared from benzylhydrazine and methylthiocarbimide, separates from benzene in rhombohedra and melts at 129° . Benzaldehydebenzyl-methylthiosemicarbazone melts at 147° .

β -Benzyl- δ -allylthiosemicarbazide, $\text{CH}_2\text{Ph}\cdot\text{N}(\text{CS}\cdot\text{NH}\cdot\text{C}_3\text{H}_5)\cdot\text{NH}_2$, separates from light petroleum in glassy prisms and melts at 61° . Benzaldehydebenzylallylthiosemicarbazone melts at $106\text{--}107^\circ$.

δ -Phenyl- β -benzylthiosemicarbazide, $\text{CH}_2\text{Ph}\cdot\text{N}(\text{CS}\cdot\text{NHPh})\cdot\text{NH}_2$, prepared from benzylhydrazine and phenylthiocarbimide, separates from alcohol in glistening leaflets and melts at 123° . Benzaldehydephenylbenzylthiosemicarbazone melts at 132° . Phenylbenzylthiosemicarbazide methyl ether is a yellow oil, which, with benzenesulphonic chloride, forms the sulphone, separating from alcohol in prisms and melting at 126° . The methyl ether condenses with benzaldehyde to form the benzylidene derivative, $\text{CH}_2\text{Ph}\cdot\text{N}(\text{C}\cdot\text{NPh}\cdot\text{SMe})\cdot\text{N}\cdot\text{CHPh}$, which crystallises in yellow needles and melts at 104° .

δ -Phenyl- β -benzylthiosemicarbazide is exceptional in undergoing transformation into δ -phenyl- α -benzylthiosemicarbazide at 130° ; the latter compound melts at 155° .

α -Benzoyl- δ -phenylsemicarbazide, $\text{NHBz}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$, prepared from benzoylhydrazide and phenylcarbimide, separates from alcohol in glistening leaflets and melts at 210° . It does not form a condensation product with benzaldehyde, nor does it reduce Fehling's solution.

β -Phenyl- δ -methylsemicarbazide hydrochloride melts at 177° . Benzaldehydephenylmethylsemicarbazone melts at $151\text{--}152^\circ$. Phenylmethylsemicarbazide methyl ether is a red oil, the main product of the condensation of which with benzaldehyde was the benzylidene derivative, $\text{SMe}\cdot\text{C}(\text{NMe})\cdot\text{NPh}\cdot\text{N}\cdot\text{CHPh}$, which melts at $136\text{--}137^\circ$.

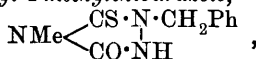
α -Phenyl- δ -methylthiosemicarbazide, prepared according to Marckwald's directions, condenses with benzaldehyde to form endothio-

diphenylmethyltriazole, $\text{MeN} \begin{array}{c} \text{CPh-NPh} \\ > \text{S} \\ \text{C}=\text{N} \end{array}$, which separates from a mixture of chloroform and alcohol in glistening, amber-coloured plates and melts at $242\text{--}243^\circ$. A. MCK.

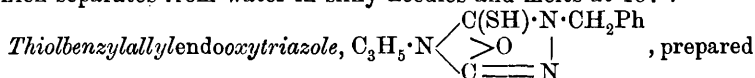
Transformations in the Urazole Series. II. MAX BUSCH and ERICH OFFERMANN (*Ber.*, 1904, 37, 2333—2338. Compare Abstr., 1902, i, 322 and preceding abstract).—The tautomeric phenomena observed by Marckwald and Sedlacek with the product obtained by the action of carbonyl chloride on phenylmethylthiosemicarbazide have been studied by the authors with the triazole derivatives. Desmotropism was noted only in the cases of those triazoles which are derived from aliphylhydrazines, whilst with derivatives of arylhydrazines, studied by Marckwald and his pupils and termed by them iminodiazolones, tautomerism was exhibited where the two isomerides could not be isolated.

5-Thiol-1-benzyl-4-methylendooxytriazole, $\text{NMe} \begin{array}{c} \text{C}(\text{SH})\cdot\text{N}\cdot\text{CH}_2\text{Ph} \\ > \text{O} \\ \text{C}=\text{N} \end{array}$, prepared from carbonyl chloride and β -benzyl- δ -methylthiosemi-

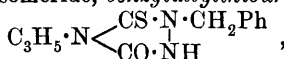
carbazine, forms tiny needles and melts at 117°. At the temperature of its melting point, or by crystallising it from hot water, or by acidifying its hot alkaline solution, it is transformed into the more stable isomeride, 1-benzyl-4-methylthiourazole,



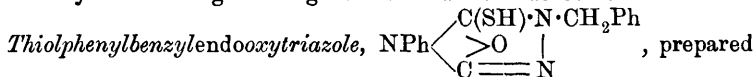
which separates from water in silky needles and melts at 157°.



from carbonyl chloride and β -benzyl- δ -allylthiosemicarbazide, crystallises in needles, melts at 108°, and readily undergoes transformation into the more stable isomeride, benzylallylthiourazole,



which crystallises in glistening needles and melts at 161°.



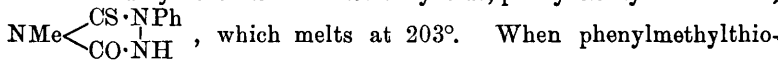
from δ -phenyl- β -benzylthiosemicarbazide and carbonyl chloride, forms slender needles and melts at 147°. At its melting point, or when crystallised from alcohol, it undergoes rearrangement into phenylbenzylthiourazole, $\text{NPh} \begin{array}{c} \text{CS} \cdot \text{N} \cdot \text{CH}_2\text{Ph} \\ | \\ \text{CO} \cdot \text{NH} \end{array}$, which forms slender, silky needles

and melts at 218°.

β -Phenyl- δ -methylthiosemicarbazide- α -carboxylic acid,



prepared from carbonyl chloride and β -phenyl- δ -methylthiosemicarbazide (compare Illgen, *Inaug. Diss. Berlin*, 1894), is readily transformed by heat into its inner anhydride, phenylmethylthiourazole,



When phenylmethylthiourazole is heated with methyl iodide at 100°, methyl mercaptan is evolved and 1-phenyl-4-methylurazole is obtained, identical with the product previously described by Busch and Heinrichs (*Abstr.*, 1901, i, 617). During the methylation, the thiourazole reacts as the tautomeric endooxytriazolethiol.

A. McK.

3:8-Diaminodiphenyleneazone. FRITZ FICHTER and PAUL DIETERLE (*Zeit. Farb. Text. Chem.*, 1904, 37, 157).—3:8-Diaminodiphenyleneazone (Ullmann and Dieterle, this vol., i, 269) condenses with benzaldehyde in alcoholic solution to form the *dibenzylidene* derivative, $\text{C}_{26}\text{H}_{18}\text{N}_4$, which crystallises from xylene in lustrous, sulphur-yellow leaflets and melts at 210°; the analogous *difurfurylidene* derivative forms yellowish-brown leaflets and melts at 207°.

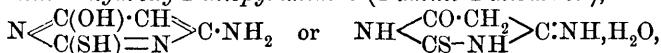
3:8-Diphenyleneazone, when diazotised in the usual way, condenses with sodium naphthionate forming a crimson dye which is directly applicable to cotton. The introduction of an azone ring into the benzidine nucleus in the ortho-position relatively to the diphenyl

linking does not therefore destroy the direct dyeing properties of the base.

W. A. D.

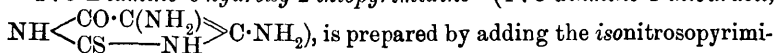
Synthesis of Xanthine Bases from Cyanoacetic Acid. Synthesis of Hypoxanthine and Adenine. WILHELM TRAUBE (*Annalen*, 1904, 331, 64—88. Compare Abstr., 1900, i, 416; 1901, i, 54).—In continuation of previous work on the synthesis of xanthine bases from cyanoacetic acid, the synthesis of hypoxanthine and adenine has now been achieved by condensing thiocarbamide (not guanidine, as in the earlier experiments) with ethyl cyanoacetate and malononitrile respectively.

4-Amino-6-hydroxy-2-thiopyrimidine (4-amino-2-thiouracil),

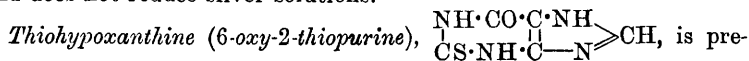


is prepared by heating at 100° a solution of sodium ethoxide in absolute alcohol with a powdered mixture of mol. proportions of thiocarbamide and ethyl cyanoacetate, when the sodium salt of the pyrimidine separates; the pyrimidine crystallises in long needles from water, and forms crystalline salts with both acids and bases. The *isonitroso*-derivative is prepared by adding sodium nitrite and acetic acid successively to a solution of the pyrimidine in alkali hydroxide, and is purified by conversion into the ammonium salt; the salts form well-developed crystals, which are fairly soluble in water.

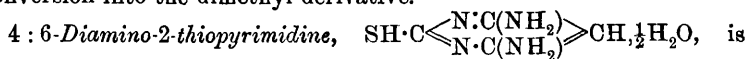
4 : 5-Diamino-6-hydroxy-2-thiopyrimidine (4 : 5-diamino-2-thiouracil,



Thiohypoxanthine (6-oxy-2-thiopurine),

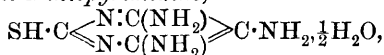


4 : 6-Diamino-2-thiopyrimidine,



melt at 280° ; it forms a crystalline *hydrochloride* and *sulphate* and an amorphous *platinichloride*, and dissolves readily in alkali hydroxides. The *isonitroso*-derivative is obtained as a green solid by adding successively sodium nitrite and acetic acid to an alkaline solution of the pyrimidine.

4 : 5 : 6-Triamino-2-thiopyrimidine,



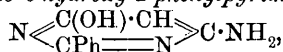
is prepared by reducing the *isonitroso*-derivative, just described, with 10 per cent. ammonium sulphide, and forms (from water) large, yellow, prismatic crystals; it forms a sparsely soluble *sulphate*, *nitrate*, and *hydrochloride*, and is also soluble in alkali hydroxides, but not in ammonia; it reduces ammoniacal silver nitrate very readily. The *monoformyl* derivative crystallises, with H_2O , in long, silky needles which soften at 140° , and is soluble both in acids and alkali hydroxides, acting towards the latter as a monobasic acid. The potassium salt, with H_2O , forms large, colourless crystals.

Thioadenine (6-amino-2-thiopurine), $\text{N} \cdot \text{C}(\text{NH}_2) \cdot \text{C} \cdot \text{NH} \begin{array}{c} \text{N} \\ \text{C}(\text{SH}) \cdot \text{N} - \text{C} - \text{N} \end{array} \rangle \text{CH}, \text{H}_2\text{O}$, is

prepared by heating the potassium salt of the formyl derivative, just mentioned, at 230° for 40 minutes, when the potassium salt of the purine is formed; it forms pale yellow, insoluble crystals, and has both acid and basic properties, being readily soluble in alkali hydroxides, and forming crystalline salts with acids, of which the *sulphate* is easily prepared. After several trials, it was found that the thio-compound could only be converted into adenine by oxidation with hydrogen peroxide in the presence of acids. The synthetical adenine was proved to be identical with the natural product by identity of water of crystallisation, and of the behaviour of the sulphate towards reducing agents.

K. J. P. O.

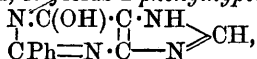
2-Phenylhypoxanthine and 2-Phenyladenine. WILHELM TRAUBE and LUDWIG HERRMANN (*Ber.*, 1904, 37, 2267—2272. Compare *Abstr.*, 1900, i, 416).—4-Amino-6-hydroxy-2-phenylpyrimidine,



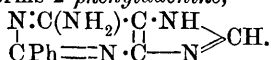
is formed by the action of sodium ethoxide and ethyl cyanoacetate on benzamidine. It crystallises in slender needles, melts at 252° , is soluble in dilute alkali hydroxides and acids, and forms a *sodium* compound and a *platinichloride*, which crystallises in long, yellow needles. The *isonitroso*-compound, obtained by acting on 4-amino-6-hydroxy-2-phenylpyrimidine, crystallises in green needles and is soluble in dilute alkali hydroxides and ammonia to solutions which slowly deposit bluish-violet, crystalline *salts*. It is soluble with decomposition in mineral acids.

Reduction of the *isonitroso*-compound with ammonium sulphide leads to the formation of 4 : 5-diamino-6-hydroxy-2-phenylpyrimidine, $\text{N} \begin{array}{c} \text{C}(\text{OH}) \cdot \text{C}(\text{NH}_2) \\ \text{CPh} = \text{N} \end{array} \rangle \text{C} \cdot \text{NH}_2$, which separates from alcohol in dark green crystals and forms a *hydrochloride*, $\text{C}_{10}\text{H}_{10}\text{ON}_4 \cdot \text{HCl}$. When

heated with formic acid, it yields 2-phenylhypoxanthine,

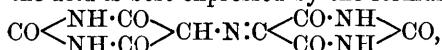


which is soluble in hot alcohol, yields a hydrochloride which is partly decomposed by water, forms an amorphous precipitate with silver nitrate in ammoniacal solution, and gives the murexide reaction. When heated with phosphorus oxychloride in a sealed tube at 140°, 2-phenylhypoxanthine yields 6-chloro-2-phenylpurine, which crystallises from alcohol in colourless, rhombic plates, and, with aqueous ammonia at 140° under pressure, forms 2-phenyladenine,

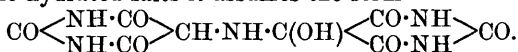


This crystallises from hot water in slender, colourless needles, forms a neutral aqueous solution, and is precipitated from its ammoniacal or nitric acid solutions by silver nitrate. G. Y.

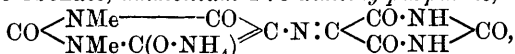
Constitution of Purpuric Acid and of Murexide. MAX SLIMMER and JULIUS STIEGLITZ (*Amer. Chem. J.*, 1904, 31, 661—679).—The generally accepted formula for purpuric acid is that proposed by Beilstein, namely, $\text{CO} \begin{array}{c} \text{NH·CO} \\ \text{NH·CO} \end{array} \text{C} \begin{array}{c} \text{NH} \\ \text{C} \end{array} \begin{array}{c} \text{CO·NH} \\ \text{CO·NH} \end{array} \text{CO}$. The present paper shows that this conception is inaccurate, and that the constitution of the acid is best expressed by the formula



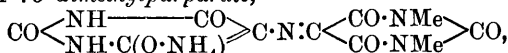
whilst in the hydrated salts it assumes the form



When 1:3-dimethyluramil is treated with alloxan in presence of ammonium carbonate, ammonium 1:3-dimethylpurpurate,

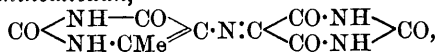


is produced, which crystallises in small, four-sided prisms and resembles ordinary murexide, but is slightly yellower in colour; when warmed with dilute hydrochloric acid, it is converted into dimethyluramil and alloxantin. By the condensation of uramil with dimethylalloxan, ammonium 1':3'-dimethylpurpurate,



is obtained, which closely resembles its isomeride, but is decomposed by dilute hydrochloric acid with formation of dialuric acid amide and tetramethylalloxantin. These results show that the purpuric acid molecule is not symmetrical, and its constitution therefore cannot be correctly represented by Beilstein's formula.

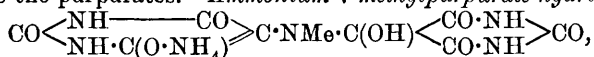
By the condensation of 5-amino-4-methyluracil with alloxan, 4-methyluraciliminoalloxan,



is obtained as a heavy, dark red precipitate. It follows, therefore, that the presence of the hydrogen attached to the carbon atom in the

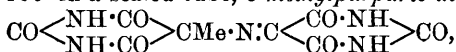
uramil group is not essential to the formation of condensation products of the nature of purpuric acid, whereas, according to Beilstein's formula, such is the case.

The so-called water of crystallisation present in ammonium purpurate hydrate (murexide) and the corresponding potassium salt is constitutional; this is shown by the fact that salts of intensely coloured purpuric acid derivatives can be prepared from 7-alkyluramils and alloxan, which cannot lose the molecule of water, but in other respects resemble the purpurates. *Ammonium 7-methylpurpurate hydrate*,



obtained by the condensation of 7-methyluramil and alloxan, crystallises in small, four-sided prisms and closely resembles ordinary murexide; this compound can also be prepared by the oxidation of 7-methyluramil with mercuric oxide, and by the action of methylamine on alloxantin. *Ammonium 7-ethylpurpurate hydrate* has similar properties.

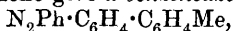
When anhydrous potassium purpurate is heated with methyl iodide for 5 hours at 100° in a sealed tube, *5-methylpurpuric acid*,



is produced. By the action of methyl iodide on silver purpurate, *O-4-methyl purpurate*, $\text{CO} \begin{array}{c} \text{NH} \text{---} \text{CO} \\ \text{NH} \cdot \text{C}(\text{OMe}) \end{array} \text{C} \cdot \text{N} \cdot \text{C} \begin{array}{c} \text{CO} \cdot \text{NH} \\ \text{CO} \cdot \text{NH} \end{array} \text{CO}$, is formed, which has a deep red colour and is very unstable. E. G.

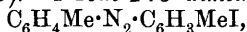
Action of Benzene on Azoxybenzene in presence of Aluminium Chloride. ERNEST BANDROWSKI and ALEXANDER PROKOPECZKO (*Bull. Acad. Sci. Cracow*, 1904, 158—162).—Azoxybenzene reacts readily with benzene in presence of aluminium chloride. The chief products are benzeneazodiphenyl and azodiphenyl. Benzenehydrazodiphenyl may be obtained by reducing benzeneazodiphenyl; it melts at 122° and yields two isomeric diacetyl derivatives, one of which crystallises in leaflets, melts at 217°, and is sparingly soluble in alcohol, whilst the other readily dissolves in that medium and forms needles which melt at 176°.

Toluene and azoxybenzene give a *benzeneazomethyldiphenyl*,



which melts at 137° together with azoditolyl, $\text{N}_2(\text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4\text{Me})_2$, which melts at 260°. *Benzenehydrazomethyldiphenyl*, $\text{N}_2\text{H}_2\text{Ph} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4\text{Me}$, melts at 102°. S. S.

Derivatives of 4'-Iodo-2:3'-dimethylazobenzene and of m-Bromiodobenzene with Polyvalent Iodine. CONRAD WILLGERODT and PAUL LEWISO (*J. pr. Chem.*, 1904, [ii], 69, 321—333. Compare this vol., i, 485).—*4'-Iodo-2:3'-dimethylazobenzene*,



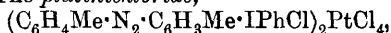
obtained by the action of potassium iodide on diazotised-4'-amino-2:3'-dimethylazobenzene, crystallises in golden needles, melts at 64°, has no odour, and is easily soluble in organic solvents, but is insoluble in water. The *iodochloride*, $\text{C}_6\text{H}_4\text{Me} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{ICl}_2$, prepared by chlor-

inating iododimethylazobenzene in chloroform solution and pouring the reaction product into petroleum, separates in red, prismatic crystals and decomposes at 101° . 4'-Iodoso-2:3'-dimethylazobenzene is formed when the iodochloride is allowed to remain in contact with 20 per cent. sodium hydroxide solution for 8 days. It is an amorphous, reddish-yellow powder, which decomposes at 273° and is soluble in alcohol, more easily so in glacial acetic acid. 4'-Iodoxy-2:3'-dimethylazobenzene, $C_6H_4Me \cdot N_2 \cdot C_6H_3Me \cdot IO_2$, is formed by the action of sodium hypochlorite solution on the iodochloride. It crystallises in prisms, melts at 180° , and explodes if rapidly heated in a capillary tube.

Phenyl-2:3'-dimethylbenzeneazophenyl-4'-iodonium chloride,



is obtained by the action of mercury diphenyl on dimethylazobenzene iodochloride in benzene solution. It forms a powder consisting of small, scarlet needles, melts at 146° , and is soluble in water, alcohol, and ether. From this iodonium chloride, the following salts have been prepared. The *bromide* crystallises in red needles and melts and decomposes at 146° . The *iodide* crystallises in microscopic needles and melts at 143° . The *platinichloride*,



crystallises in small, yellow leaflets and decomposes at 168° . The *dichromate* crystallises in small, scarlet needles and melts and decomposes at 178° .

Di-m-bromophenyliodonium hydroxide, $I(C_6H_4Br)_2 \cdot OH$, is obtained by the action of silver oxide on *m*-bromoiodobenzene. The following salts have been prepared. The *chloride* crystallises in slender needles and melts at 207° ; the *bromide* forms small needles and melts at 178° ; the *iodide* crystallises in slender needles and melts at 154° ; the *platinichloride* separates from alcohol in glistening leaflets and melts and decomposes at 178° ; the *dichromate* crystallises in yellow needles and decomposes at 181° .

Phenyl-m-bromophenyliodonium hydroxide, $C_6H_4Br \cdot IPh \cdot OH$, is slightly alkaline in aqueous solution; the *chloride* forms white needles and melts at 191° ; the *bromide* crystallises in needles and melts at 169° ; the *iodide* crystallises in needles and melts at 146° ; the *platinichloride* forms a yellow, crystalline precipitate and melts and decomposes at 181° ; the *mercurichloride* crystallises in white needles and melts at 130° ; the *dichromate* is a yellow, crystalline powder, which melts and decomposes at 137° .

In aqueous solution, *m-bromophenyl-p-tolyliodonium hydroxide* has a slight alkaline reaction; the *chloride* crystallises in small needles and melts at 174.5° ; the *bromide* crystallises in white needles and melts at 175° ; the *iodide* forms yellow needles and melts and decomposes at 139° . The *platinichloride* crystallises in yellow needles and melts and decomposes at 182.5° ; the *mercurichloride* forms white needles and melts at 139° .

m-Bromophenyl-o-tolyliodonium hydroxide is only known in its slightly alkaline, aqueous solution; the *chloride* is a yellow, crystalline powder which melts at 170° ; the *bromide* is a white, crystalline precipitate which melts at 185° ; the *platinichloride* crystallises in yellow leaflets and melts and decomposes at 182° ; the *mercurichloride*

melts at 110—115°; the *nitrate* is a white, crystalline precipitate which melts and decomposes at 181°.

m-Bromophenyl-*a*-naphthylidonium hydroxide has a slight alkaline reaction in aqueous solution; the *chloride* forms small, white needles and melts at 159°; the *bromide* crystallises in small needles and melts at 156°; the *iodide* is a crystalline powder of small needles and melts and decomposes at 133°; the *platinichloride* crystallises in golden needles and melts at 158°; the *mercurichloride* crystallises in prisms and melts at 278°; the *dichromate* forms a powder of small, yellow needles and melts and decomposes at 132°. G. Y.

Action of Diazobenzene Chloride on Diphenylamine. LÉO VIGNON and ADOLPHE SIMONET (*Compt. rend.*, 1904, 138, 1104—1105).—Phenyldiazaminobenzene, $\text{NPh}\cdot\text{N}\cdot\text{NPh}_2$, prepared by diazotising aniline hydrochloride in the presence of diphenylamine, is insoluble in water, sparingly soluble in alkaline solvents, readily so in alcohol, ether, or benzene, crystallises in bright yellow spangles from alcohol and water, melts at 47°, decomposes slowly at the ordinary temperature, rapidly at 100°, and explosively at 175—180°. It is readily decomposed by acids into nitrogen, diphenylamine, and phenol, and converted into the corresponding aminoazo-compound when heated with excess of diphenylamine and a little diphenylamine hydrochloride. The *hydrochloride* is violet, melts with decomposition at 135°, decomposes in the air, and is dissociated in water. The *platinichloride* decomposes without melting at 100—105°. M. A. W.

[Azo-derivatives of Phenylanthranilic Acid.] FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 150469).—Benzeneazodiphenylamine-*o*-carboxylic acid (this vol., i, 353) may also be regarded as benzeneazophenylanthranilic acid. Unlike phenylanthranilic acid, it does not yield an acridone derivative when heated with fuming sulphuric acid at 90—95°, but forms a *sulphonic acid*, which is yellow, dissolves in water, and forms yellow salts. Similar dyes are obtained from toluene-*o*-azo-*o*-tolylanthranilic acid (toluene-*o*-azo-*o*-tolylphenylamine-*o*-carboxylic acid) and toluene-*p*-azo-*p*-tolylanthranilic acid.

C. H. D.

Diazoamino-compounds. LOUIS MEUNIER (*Bull. Soc. chim.*, 1904, [iii], 31, 641—644).—5 : 5'-Dinitro-2 : 2'-diazoaminotoluene, produced by the action of sodium nitrite (1 mol.) on 5-nitro-*o*-toluidine dissolved in acetic acid, separates from acetone in golden-yellow crystals and melts at 237°.

The three diazoaminobenzenedisulphonic acids were prepared by dissolving the corresponding anilinedisulphonic acids (2 mols.) in water containing sodium carbonate (1 mol.) and adding to this sodium nitrite (1 mol.) and sulphuric acid ($\frac{1}{2}$ mol.). The sodium salts so formed were obtained as greenish-yellow, hygroscopic precipitates by the addition of ammonium chloride. They react with copper powder to form cuprous derivatives which produce red solutions in water and have the formula $\text{SO}_3\text{Na}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{NCu}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{Na}$. Solutions of

The following table shows the relations of vegetable proteids and their derivatives to solvents :

| | Dilute alcohol. | Water at 100°. | Cold water. | 10 % NaCl. | Pan- creatic juice. | KOH | No. of positive signs. |
|--------------------------|--------------------|-------------------|----------------|---------------|---------------------------|-----|------------------------------|
| 1. Peptone and albumoses | + | + | + | + | + | + | 6 |
| 2. Albumin ... | - | - | + | + | + | + | 4 |
| 3. Globulin ... | - | - | - | + | + | + | 3 |
| 4. Gliadin ... | + | - | - | - | + | + | 3 |
| 5. Casein ... | - | - | - | - | + | + | 2 |
| 6. Nuclein ... | - | - | - | - | - | + | 1 |

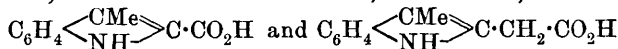
N. H. J. M.

White and Yoke of Egg ; Action of Hydrogen Sulphide on Unbroken Eggs. EGIDIO POLLACCI (*Gazzetta*, 1904, 34, i, 278—286).—By boiling white and yoke of egg separately with water, the author finds that they both lose a considerable proportion of their sulphur, showing that the proteids are broken down and the nutritive value of the egg diminished.

On allowing an unbroken egg to remain for 24 hours in a closed vessel full of hydrogen sulphide, it was found, on breaking the egg, that the white had lost its natural viscosity and had become limp like water, and that it had assumed a yellowish-green colour and a fœtid odour ; the yolk, on the other hand, had become of a very dark chocolate colour. The albuminates, especially those of sodium and calcium, present in the white are hence decomposed into the corresponding sulphides, together with mercaptan-substances ; the dark colour of the yolk is due to the formation of ferric sulphide.

The reactions of the white and yolk of egg are given in tabular form.
T. H. P.

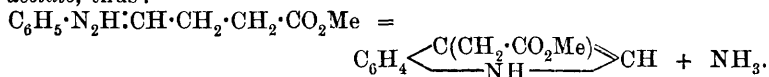
Constitution of the Indole Group in Albumin. (Synthesis of the so-called Scatolecarboxylic Acid.) Source of Kynurenic Acid. ALEXANDER ELLINGER (*Ber.*, 1904, 37, 1801—1808).—The decomposition products from proteids which contain the indole grouping are, besides indole itself, scatole, scatolecarboxylic acid, and scatoleacetic acid ; to the two latter substances, the formulæ,



respectively have been assigned by Nencki and others, whilst to the parent substance, tryptophan, the formula for α -amino- α -scatoleacetic acid, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CMe} \\ \diagup \quad \diagdown \\ \text{NH} \end{array} \text{C} \cdot \text{CH}(\text{NH}_2) \cdot \text{CO}_2\text{H}$, has been given (compare Hopkins and Cole, *Abstr.*, 1902, i, 193). Wislicenus and Arnold have, however, synthesised scatolecarboxylic acid of the constitution $\text{C}_6\text{H}_4 \begin{array}{c} \text{CMe} \\ \diagup \quad \diagdown \\ \text{NH} \end{array} \text{C} \cdot \text{CO}_2\text{H}$, and this substance is not identical with that obtained from proteids. On this ground, and also from the results of biological experiments conducted by the author and Gentzen (*Abstr.*,

1903, i, 781), the constitution of scatolecarboxylic acid has been studied afresh and is shown to be $C_6H_4 \begin{smallmatrix} \text{C}(\text{CH}_2 \cdot \text{CO}_2\text{H}) \\ \text{NH} \end{smallmatrix} \text{CH}$.

Itaconic acid was converted into aconic acid (Metzing, *Inaug. Diss.*, Königsberg, 1901), which, on being boiled with water, yielded β -aldehydopropionic acid (von Ungern-Sternberg, *Inaug. Diss.*, Königsberg, 1904. Compare also Perkin and Sprankling, *Trans.*, 1899, 75, 11). The latter was then converted by the silver salt method into its methyl ester, the phenylhydrazone of which, when boiled for several hours with alcoholic sulphuric acid, yielded *methylindole-3-acetate*, thus:



The acid obtained from the hydrolysis of this ester was identical in melting point and crystalline form with that prepared by E. and H. Salkowski from proteids.

Physiological experiments on dogs showed that tryptophan is converted in the organisms into kynurenic acid. Since the latter has been shown by Camps (Abstr., 1901, i, 751) to be 4-hydroxyquinoline-3-carboxylic acid, $C_6H_4 \begin{smallmatrix} \text{C}(\text{OH}) \cdot \text{C} \cdot \text{CO}_2\text{H} \\ \text{N} = \text{CH} \end{smallmatrix}$, the formula for tryptophan is most probably $NH \begin{smallmatrix} \text{C}_6H_4 \\ \text{CH} \end{smallmatrix} \text{C} \cdot CH(\text{CO}_2H) \cdot CH_2 \cdot NH_2$.

A. McK.

The Carbohydrate Group in Serum-globulin, Serum-albumin, and Egg-albumin. EMIL ABDERHALDEN, PETER BERGELL, and THEODOR DÖRPINGHAUS (*Zeit. physiol. Chem.*, 1904, 41, 530—534).—Serum-globulin yields a very small quantity (about 0.1 per cent.) of dextrose, identified by its osazone; whether traces of glucosamine are also present is doubtful. Whether the serum-globulin really contains a dextrin-like substance in its molecule which yields the sugar is uncertain; the variable amount of sugar obtained rather points to an admixture. Serum-albumin similarly yields a small amount of sugar, but after repeated crystallisation there is no evidence of any at all. The small amount of reducing material obtained from egg-albumin is glucosamine; its amount is variable. Here also mechanical admixture is the probable explanation of its presence. W. D. H.

Organic Chemistry.

Optical Investigation of Naphtha and of its Distillation Products. M. A. RAKUSIN (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 554—559).—The author's measurements show that both the colourless and the yellow distillates obtained from naphtha give rotations varying from +0.2 to +2.3 divisions of the Soleil-Ventzke scale in a tube 200 mm. long, the highest value being given by yellow cylinder oil from Baku naphtha. "Benzine" and petroleum from Grosny naphtha and also the yellow American cylinder oil "Viscolite" (of the Vacuum Oil Company) exhibit dextro-rotations. T. H. P.

$\alpha\gamma$ -Pentadiene. N. WOSNESENSKY (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 532—536).— $\beta\delta$ -Dibromopentane (see Poray-Koschitz, this vol., i, 363) loses its bromine when treated with quinoline, yielding $\alpha\gamma$ -pentadiene, $\text{CHMe}:\text{CH}:\text{CH}:\text{CH}_2$, which is a mobile liquid with a characteristic odour, boils at 41.5—43°, and has sp. gr. 0.6952° at 0°/0°. The corresponding tetrabromide, $\text{C}_5\text{H}_8\text{Br}_4$, crystallises from alcohol in shining plates melting at 114°. Oxidation of the pentadiene with permanganate gives rise to acetic acid. T. H. P.

Decomposition of Ethylene and Ethylidene Dichlorides by Heat. HEINRICH BILTZ and ERNST KÜPPERS (*Ber.*, 1904, 37, 2398—2423. Compare Abstr., 1903, i, 1).—The decomposition of ethylene and ethylidene dichlorides into chloroethylene and hydrogen chloride takes place at 300—450° under the catalytic action of the glass walls of the reaction vessel. At 300—400°, the dichlorides are in varying equilibrium with their decomposition products, the amount of the latter formed increasing with the rise in temperature, but also varying with the extent of surface of the glass vessel. Above 400°, the decomposition takes place completely.

One glass vessel was found to have no catalytic action, as with the dichlorides at 401° for 120 minutes, and at 448° for 60 minutes, no increase of pressure was observed. G. Y.

Action of the Simplest Secondary Iodide on Magnesium. WLADIMIR TSCHELINZEFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 549—554).—When magnesium and isopropyl iodide interact, besides the normal formation of organo-magnesium compound, there takes place also a reaction of elimination and reduction, thus: $2\text{CHMe}_2\text{I} + \text{Mg} = \text{MgI}_2 + \text{CH}_2:\text{CHMe} + \text{CH}_2\text{Me}_2$, propane and propylene being formed. This reaction accounts for about 41 per cent. of the isopropyl iodide, whilst 1.47 per cent. undergoes the following decomposition: $2\text{CHMe}_2\text{I} + \text{Mg} = \text{MgI}_2 + 2\text{CH}_2:\text{CHMe} + \text{H}_2$. T. H. P.

Preparation of Alcohol from Acetylene. LA SOCIÉTÉ S. JAY & Co. (D.R.-P. 149893).—A mixture of 1 vol. of acetylene with 4 vols. of hydrogen is passed into a specially constructed apparatus of glass

or porcelain, and is there mixed with ozonised oxygen, the whole being cooled by means of solid carbon dioxide. Combination readily takes place, with the formation of alcohol, inactive oxygen escaping through a mercury outlet. A suitable form of apparatus is described and figured.

C. H. D.

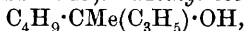
Preparation of Primary Alcohols by means of the Corresponding Acids. LOUIS BOUVEAULT and GUSTAVE BLANC (*Bull. Soc. chim.*, 1904, [iii], 31, 748—750. Compare Abstr., 1903, i, 597 and 673).—The method of reduction previously described (*loc. cit.*) is found to be applicable to substituted acetic acids of the types $\text{CHRR}^1\cdot\text{CO}_2\text{H}$ and $\text{CRR}^1\text{R}^{11}\cdot\text{CO}_2\text{H}$.

α -Methyloctoic acid, prepared from octoic acid obtained from castor oil, boils at 136° under 17 mm. pressure and has a sp. gr. 0.9098 at $0^\circ/4^\circ$. The ethyl ester has a fruity odour, boils at 99° under 13 mm. pressure, has a sp. gr. 0.8759 at $0^\circ/4^\circ$, and on reduction furnishes α -methyloctyl alcohol, a liquid of pleasant odour, boiling at 98 — 99° under 16 mm. pressure and having a sp. gr. 0.8418 at $0^\circ/4^\circ$.

Ethyl $\alpha\alpha$ -dimethylbutyrate is a liquid of pleasant, slightly camphoraceous odour; it boils at 141 — 142° , has a sp. gr. 0.883 at $0^\circ/4^\circ$, and on reduction furnishes $\alpha\alpha$ -dimethylbutyl alcohol. The latter has a camphoraceous odour, boils at 135° , does not solidify when cooled to -15° , and has a sp. gr. 0.844 at $0^\circ/4^\circ$.

Ethyl campholate, $\begin{array}{c} \text{CHMe}\cdot\text{CMe}_2 \\ | \\ \text{CH}_2 \end{array} > \text{CMe}\cdot\text{CO}_2\text{Et}$, on reduction furnishes a *campholyl alcohol*, which has an odour similar to that of borneol, crystallises in white needles, melts at 60° , and boils at 213° (compare Errera, Abstr., 1893, 108; 1894, 202); the *phenylurethane* melts at 45° and is readily soluble in organic solvents. T. A. H.

Methylisobutylallylcarbinol. DIMITRI MARKO (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 544—549).—*Methylisobutylallylcarbinol*,



prepared by decomposing with water the compound obtained by the action of zinc and allyl iodide (2 mols.) on methylisobutyl ketone (1 mol.), is a colourless liquid with a caustic taste and a faint odour of turpentine; it boils at 173.7° , is readily soluble in alcohol or ether, does not crystallise even at -25° , and has the sp. gr. 0.83545 at $20^\circ/0^\circ$, 0.83652 at $20^\circ/20^\circ$, 0.82632 at $30^\circ/0^\circ$, and 0.82748 at $30^\circ/30^\circ$. Its *acetyl* derivative was prepared and analysed. On oxidation with permanganate, methylisobutylallylcarbinol yields: (1) $\alpha\beta\delta$ -trihydroxy- $\delta\zeta$ -dimethylheptane, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$, which is an uncrystallisable, syrupy liquid soluble in water, alcohol, or ether; a mixture of its diacetyl and triacetyl derivatives was prepared. (2) β -Hydroxy- $\beta\delta$ -dimethylhexoic acid,



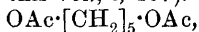
was obtained as a thick, uncrystallisable syrup soluble in water, alcohol, or ether; its *calcium*, *silver*, and *zinc* salts were prepared and analysed.

All the methylbutylallylcarbinols are now known, their boiling points and sp. grs. being as follows:

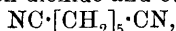
| | B. p. at 760 mm. pressure. | Sp. gr. at 20°/0°. | Sp. gr. at 20°/20°. |
|------------------------------------|----------------------------------|-----------------------|------------------------|
| Methylbutylallyl- carbinol with | | | |
| <i>n</i> -Butyl | 179·1° | 0·84412 | 0·84497 |
| <i>iso</i> Butyl | 173·7 | 0·83545 | 0·83652 |
| <i>sec.</i> -Butyl | 174·9 | 0·85438 | 0·85526 |
| <i>tert.</i> -Butyl | 168·4 | 0·85535 | 0·85639 |

T. H. P.

Syntheses of Amylene $\alpha\epsilon$ -Glycol, of the Nitrile, and of Pimelic Acid. JULES HAMONET (*Compt. rend.*, 1904, 139, 59—61. Compare Abstr., 1901, i, 187, 247; this vol., i, 467).— $\alpha\epsilon$ -Diacetoxypentane,



is a colourless liquid with a fruity odour, which boils at 241° under 760 mm. pressure, when placed in a freezing mixture, forms white crystals melting at 2°, has a sp. gr. 1·021 at 18°, and yields, on saponification, *amylenes $\alpha\epsilon$ -glycol*, $\text{OH} \cdot [\text{CH}_2]_5 \cdot \text{OH}$, in the form of a thick liquid resembling glycerol; this has a burning and bitter taste, boils at 238—239° under 760 mm. or at 155° under 31 mm. pressure, has a sp. gr. 0·994 at 18°, and solidifies, but does not crystallise, in a mixture of solid carbon dioxide and ether. *Pimelonitrile*,



prepared by the action of potassium cyanide on di-iodopentane at 85°, is a mobile liquid, which boils at 175—176° under 14 mm. pressure, has a sp. gr. 0·949 at 18°, does not solidify in a mixture of solid carbon dioxide and ether, and yields pimelic acid when heated in a sealed tube with concentrated hydrochloric acid at 100°. M. A. W.

Action of Sulphuric Acid on Certain Glycerols obtained by the Oxidation of Unsaturated Tertiary Alcohols of the Series $\text{C}_n\text{H}_{2n-1}\text{OH}$, containing One Allyl Radicle. DMITRI WAGNER, VIKTOR LWOW, and ALEXANDR BENING (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 539—544. Compare Petchnikoff, Abstr., 1901, i, 183, and 1902, i, 338).—The authors have isolated the alcohol oxides formed by the action of dilute sulphuric acid on hydroxymethylethylallylcarbinol, dihydroxymethylpropylallylcarbinol, and dihydroxymethyl-*n*-butylallylcarbinol. The three compounds obtained, which have the formulæ $\text{C}_7\text{H}_{14}\text{O}_2$, $\text{C}_8\text{H}_{16}\text{O}_2$, and $\text{C}_9\text{H}_{18}\text{O}_2$ respectively, are colourless liquids moderately soluble in water, alcohol, or ether; their constants are as follows:

| | Boiling point (corr.). | Difference. | Sp. gr. at 0°/0°. | Sp. gr. at 20°/0°. |
|---|------------------------------|-------------|----------------------|-----------------------|
| $\text{C}_7\text{H}_{14}\text{O}_2$ | 204·5° | 15·5° | 1·00076 | 0·98677 |
| $\text{C}_8\text{H}_{16}\text{O}_2$ | 220·0 | 14·8 | 0·99413 | 0·97968 |
| $\text{C}_9\text{H}_{18}\text{O}_2$ | 234·8 | | 0·95910 | 0·95910 |

T. H. P.

Method of Characterising the Fatty Acids. RENÉ LOCQUIN (*Compt. rend.*, 1904, 138, 1274—1276).—The method consists in converting the fatty acid, $R \cdot CO_2H$, by means of chloroacetone into the ketonic ester, $CH_3 \cdot CO \cdot CH_2 \cdot CO_2R$, and transforming this into the corresponding semicarbazone. The theoretical quantity of sodium is added to the acid (1 mol.) dissolved in anhydrous ether, and chloroacetone (1 mol.) is then added. After evaporating off the ether, the residue is heated at $120-130^\circ$, when the reaction $CH_3 \cdot CO \cdot CH_2Cl + R \cdot CO_2Na = CH_3 \cdot CO \cdot CH_2 \cdot CO_2R + NaCl$ takes place. After separation of the ester, it is treated with semicarbazide in acetic acid solution. The semicarbazones derived from the various fatty acids crystallise well and can be readily recognised.

H. M. D.

Some Cuprous Salts. ALEXANDRE JOANNIS (*Compt. rend.*, 1904, 138, 1498—1500. Compare Abstr., 1903, ii, 371).—The author has prepared the cuprous salts of formic and benzoic acids by allowing the ammonium salt of the acid dissolved in liquid ammonia to react with cuprous oxide in a sealed apparatus from which all air and moisture have been removed. The cuprous salt is recrystallised from liquid ammonia, and the crystals washed with the same solvent until a compound of constant composition is obtained. *Cuprous formate*, $Cu_2(CHO_2)_2 \cdot 4NH_3 \cdot \frac{1}{2}H_2O$, is a pale blue substance, which becomes deep blue in contact with moist air and brownish-black in dry air; it is decomposed by dilute acids, giving yellow cuprous oxide. *Cuprous benzoate*, $Cu_2(PhCO_2)_2 \cdot 5NH_3$, is a bluish-white, crystalline substance, very unstable in air.

M. A. W.

Auto-hydrolysis of Crude Animal Fats. PETER PASTROVICH (*Monatsh.*, 1904, 25, 355—364. Compare Abstr., 1903, ii, 249).—In an emulsion of crude tallow with water at 35° , the fat is hydrolysed by the proteid present in the membrane which surrounds the tallow. The presence of this membrane together with water increases the acid number to a considerable degree; the increase is much greater with 10 per cent. than with 5 per cent. of membrane. The auto-hydrolysis of tallow is diminished by the presence of small quantities of mineral acids or a 2 per cent. solution of chloral hydrate, and is almost completely stopped by addition of a 2 per cent. solution of mercuric chloride. Traces of ammonia or alkali hydroxides favour, but larger quantities diminish, the hydrolysis.

The increase of the acid number is found to differ with various parts of the tallow, and to be greatest for that part which contains most olein. It is also affected by the addition of other fats.

G. Y.

[Iodochlorides of Oleic Acid and its Analogues.] AKTIENGESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 150434).—It is not possible to prepare salts of iodo-fatty acids by the saponification of the iodine derivatives of fats, on account of the removal of iodine. Oleic and other unsaturated fatty acids, however, combine readily with iodine chloride, and the acids thus obtained readily form solid salts with inorganic bases, containing 10—25 per cent. of iodine.

These salts are almost tasteless, and find therapeutic application. The patent contains details of the preparation of a number of salts of chloriodo-fatty acids. C. H. D.

Method of Resolving Fermentation Lactic Acid into its Optically Active Components. ÉMILE JUNGLEISCH (*Compt. rend.*, 1904, 139, 56—59).—Ordinary quinine lactate of commerce is obtained by dissolving in its own weight of 70 per cent. alcohol a mixture of fermentation lactic acid and its equivalent of quinine; the product consists of crystalline needles of the racemic lactate containing H_2O . If, however, these crystals are left in contact with the mother liquor in a closed vessel, they slowly disappear, and octahedral crystals are formed; these are removed and the residue similarly treated. The octahedral crystals consist of quinine *d*-lactate; the *l*-lactate remains in solution and can be isolated in the form of long, silky needles containing $\frac{1}{2}\text{H}_2\text{O}$. Quinine *d*-lactate is dimorphous, crystallising in slender needles from hot concentrated solutions, or in octahedral crystals from warm or cold solutions; the needles change into the octahedral form at the ordinary temperature, whilst the converse change takes place if the octahedral crystals are heated at 150° . Wyruboff has determined the crystallographical constants of the octahedral crystals; they are pseudo-quadratic [$a:c = 1:1.8103$]. The quinine lactate prepared from the lactic acid extracted from meat juice is identical with the quinine *d*-lactate prepared as above.

M. A. W.

Action of Iodine on Dehydroacetic Acid in Pyridine Solution. GIOVANNI ORTOLEVA and G. VASSALLO (*Gazzetta*, 1904, 34, i, 342—347. Compare Abstr., 1902, i, 54, 674, and Abstr., 1903, i, 851).—The action of iodine on a pyridine solution of dehydroacetic acid mixed with alcohol yields two new compounds.

(1) A *compound*, $\text{C}_{13}\text{H}_{14}\text{O}_4\text{NI}$, which crystallises from water in shining, grey scales melting and decomposing at 234° ; it is slightly soluble in acetic acid or acetic anhydride, and more so in concentrated hydrochloric acid, from which it crystallises unchanged; the addition of silver nitrate to its aqueous solution precipitates the whole of the iodine; concentrated sulphuric acid decomposes it with elimination of iodine and hydriodic acid, whilst when heated with moist oxide of silver, the silver is deposited in the form of a mirror; dilute aqueous solutions of alkali hydroxides or carbonates colour it yellow in the cold, but when heated they dissolve it, giving red solutions, from which it is in great part precipitated unaltered by the addition of sulphuric acid. If, however, it is dissolved in warm 50 per cent. potassium hydroxide solution, which is then, cautiously and with cooling, acidified with dilute sulphuric acid, two substances are obtained: (a) a *compound*, $\text{C}_{21}\text{H}_{19}\text{O}_8\text{N}$, crystallising from water in shining, white scales, which begin to darken at 220° , and are completely carbonised without melting at 270° ; with ferric chloride, its aqueous solution gives a violet coloration. (b) A small quantity of a substance melting at 189 — 190° , which is probably the triacetic acid obtained by Collie (*Trans.*, 1891, 59, 617).

(2) A compound, $C_{16}H_{14}O_8$, which crystallises from a mixture of chloroform and benzene in small tufts of long, white needles, soluble in acetic acid, and melting and decomposing at $214-215^\circ$; it dissolves in potassium hydroxide solution with formation of a reddish-violet coloration, and, on heating the liquid, it decomposes with evolution of acetone; its aqueous solution has a faint acid reaction and readily decolorises permanganate. With bromine in chloroform solution, it yields a bromide which melts and decomposes at $153-154^\circ$ and decolorises permanganate; nitrate of silver removes the bromine from it. T. H. P.

Preparation of α -Mono-substituted Acetoacetic Esters
RENÉ LOCQUIN (*Bull. Soc. chim.*, 1904, [iii], 31, 757-760. Compare Abstr., 1901, i, 311; 1902, i, 704; 1903, i, 63, 142, and this vol., i, 552).—The author draws attention to the precautions which must be observed in the preparation of these esters in order to ensure a good yield.

Ethyl isoamylacetoacetate, $CMe_2 \cdot CH \cdot CH_2 \cdot CH_2 \cdot CHAc \cdot CO_2Et$, now obtained for the first time in a pure state by the use of synthetic isoamyl iodide (compare this vol., i, 546), is a mobile liquid which boils at $114-115^\circ$ under 12 mm. pressure and has a sp. gr. 0.957 at $0/4^\circ$.

Ethyl sec.-octylacetoacetate, $C_6H_{13} \cdot CHMe \cdot CHAc \cdot CO_2Et$, obtained by the use of sec.-octyl iodide, prepared by Bouï's method (*Ann. Chim. Phys.*, 1855, [iii], 44, 128) from the octyl alcohol of castor oil, is a slightly viscous liquid which boils at 152° under 17 mm. pressure and has a sp. gr. 0.944 at $0/4^\circ$. T. A. H.

Preparation of Stearolactone. ALEXIS A. SHUKOFF (D.R.-P. 150798).—Stearolactone is obtained by the action of sulphuric acid on oleic, isooleic, elaidic, sulphostearic, and hydroxystearic acids, or mixtures of such acids, when at least 1 mol. of concentrated sulphuric acid is employed for each mol. of oleic acid at a temperature of $60-90^\circ$. C. H. D.

Camphocarboxylic Acid, its Salts, Esters, and Ester Salts.
JULIUS W. BRÜHL and H. SCHRÖDER (*Ber.*, 1904, 37, 2512-2524).—The following results were obtained in a series of physical chemical measurements on camphocarboxylic acid, its salts, esters, and ester salts. Molecular weight determinations show camphocarboxylic acid to be largely bimolecular in benzene and ethereal solutions, unimolecular, however, in methyl alcohol and water. Its esters are unimolecular, not only in benzene and alcohol, but also in the solid state, whilst the sodium salts of methyl and ethyl camphocarboxylate are ter- or quadri-molecular in benzene and ether, actually ionised, on the other hand, in methyl alcohol. In benzene or ethereal solution, neither camphocarboxylic acid nor its salts nor ester salts behave as electrolytes. In methyl alcohol, however, the sodium salts of both camphocarboxylates and methyl camphocarboxylate behave normally as electrolytes. The rate of the autohydrolysis of the ester salts in aqueous solution has been investigated; in absolute methyl alcohol, however, the ester remains unchanged. E. F. A.

Products of Decomposition of Bromosuccinic Acid and its Salts in Aqueous Solution. WOLF J. MÜLLER and F. SUCKERT (*Ber.*, 1904, 37, 2598—2604).—Malic and fumaric acids were estimated by weighing the dry barium salts from a known weight of bromosuccinic acid; the excess of weight above that calculated for barium fumarate represented the additional water contained in the malate, the weight of which could thus be calculated.

The percentage of fumaric acid increased with the concentration, although not according to a linear law, with the proportion of hydrochloric acid added as catalyst, and with the concentration of the bromosuccinic acid; the proportion of fumaric acid also showed a marked increase when the temperature was raised to 100°. Thus the percentage of fumaric acid from *N*/20 bromosuccinic acid was 9.57 at 75° and 11.33 at 100°, but 17.61 and 19.45 in presence of *N*/10 HCl at 75° and 100° respectively. The salts of bromosuccinic acid give only malic acid when hydrolysed, and no fumaric acid. T. M. L.

New Synthesis of *αα*-Dimethyladipic Acid. GUSTAVE BLANC (*Compt. rend.*, 1904, 139, 65—67).—In addition to the synthesis of *αα*-dimethyladipic acid already given (compare this vol., i, 369), the author has synthesised it from *αα*-dimethyl- γ -butyrolactone by the following method. The lactone was converted by the action of phosphorus pentabromide and subsequent treatment with alcohol into ethyl γ -bromo-*αα*-dimethylpropionate, $\text{CO}_2\text{Et}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$, boiling at 100° under 10 mm. pressure and condensing with the sodium derivative of ethyl cyanoacetate to give ethyl δ -cyano-*αα*-dimethyl adipate, $\text{CO}_2\text{Et}\cdot\text{CMe}_2(\text{CH}_2)_2\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$, boiling at 205—210° under 15 mm. pressure and on hydrolysis with alcoholic potash yielding the acid, $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})_2$, melting at 167—168° already obtained by oxidising dihydroisolauroic acid (compare Abstr., 1900, i, 329); this acid loses CO_2 on heating at 180°, and is quantitatively converted into *αα*-dimethyl adipic acid melting at 87—88°. The *αα*-dimethyl- γ -butyrolactone used in this synthesis was obtained by reducing *αα*-dimethylsuccinic anhydride with sodium and alcohol and is identical with the compound obtained by Blaise (Abstr., 1903, i, 604) from β -iodo-*αα*-dimethylglutaric acid.

In view of these facts, the author suggests that the lactone, boiling at 207°, obtained by Perkin (compare Trans., 1901, 81, 257) by heating *αα*-dimethylglutaconic acid and treating the unsaturated acid thus obtained with dilute sulphuric acid is *isohexolactone*, which boils at 207°, and not *αα*-dimethyl- γ -butyrolactone as stated. M. A. W.

Hæmatin. WILLIAM KÜSTER and KARL HAAS (*Ber.*, 1904, 37, 2470—2473. Compare Abstr., 1902, i, 845).—*α*-Methyl- β -propylmaleic anhydride, $\text{C}_8\text{H}_{10}\text{O}_3$, prepared by combining hydrogen cyanide with cooled ethyl propylacetoacetate, hydrolysing, and distilling the methylpropylmalic acid obtained, is purified by fractional distillation or by means of the barium salt, and forms a mobile, slightly yellow, highly refractive liquid boiling at 241—242° (corr.), and has a sp. gr. 1.098 at 15°. It is almost insoluble in cold water, but dissolves

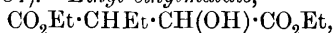
readily in alcohol, ether, chloroform, benzene, or ethyl acetate. The barium salt, $C_8H_{10}O_4Ba, H_2O$, forms pearly leaflets.

Alcoholic ammonia at 130° converts it into the imide, $C_8H_{11}O_2N$, crystallising from dilute ammonia after repeated treatment with animal charcoal in long, silky-white needles, and melting at $56-57^\circ$ and subliming without decomposition. It dissolves readily in organic solvents, sparingly in water. Its odour resembles that of iodoform.

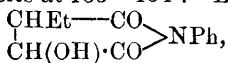
The oxidation of hæmopyrrole (Nencki and Zalesky, Abstr., 1901, i, 434) yields an imide melting at $63-64^\circ$ and having the odour of iodoform, decomposing more readily than the synthetic imide; it may perhaps be an isomeride.

Methylisopropylmaleimide melts at $44-45^\circ$ and closely resembles the *n*-propyl compound in appearance and odour. A third isomerid, xeronimide, is under investigation. C. H. D.

Ethylmalic Acid. FRITZ FICHTER and MAX GOLDBABER (*Ber.*, 1904, 37, 2382—2384).—*Ethyl ethylmalate*,



prepared by reducing ethyl oxalacetate with aluminium in moist ethereal solution, boils at $133-135^\circ$ under 12 mm. pressure. The acid, $C_6H_{10}O_5$, crystallises from a mixture of ether and light petroleum in colourless prisms and melts at $133-134^\circ$. *Ethylmalanil*,



crystallises from water in colourless, flaky needles and melts at $142-143^\circ$. *Ethylmalanilide*, $\begin{array}{c} CHEt \cdot CO \cdot NPh \\ CH(OH) \cdot CO \cdot NPh \end{array}$, is insoluble in

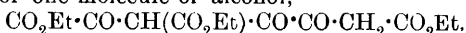
water, crystallises from alcohol in minute needles, and melts at $203-204^\circ$. α -*Ethylumbelliferone*, $HO \cdot C_6H_3 \cdot \begin{array}{c} CH : CEt \\ O - CO \end{array}$, prepared by condensing the acid with resorcinol and sulphuric acid, crystallises from water in minute, white, glistening needles, melts at $123-124^\circ$, gives blue, fluorescent solutions, and reduces Fehling's and ammoniacal silver solutions. Dry distillation of the acid gave chiefly methylcitraconic acid.

Methylcitraconanil, $\begin{array}{c} CEt \cdot CO \\ CH - CO \end{array} > NPh$, crystallises from alcohol or dilute acetic acid in pale yellow, felted needles and melts at $108-109^\circ$. The dibromide, *ethyl dibromosuccinanil*, $\begin{array}{c} CBrEt \cdot CO \\ CHBr \cdot CO \end{array} > NPh$, crystallises from acetic acid in colourless needles and melts at $164-165$. *Anilino-methylcitraconanil*, $\begin{array}{c} CEt \cdot CO \\ NPh \cdot C - CO \end{array} > NPh$, crystallises from alcohol in glistening, yellow flakes and melts at $113-114^\circ$.

Small quantities of methylitaconic and methylmesaconic acids are also produced in the distillation of ethylmalic acid. T. M. L.

Product of the Spontaneous Change of Ethyl Oxalacetate. LOUIS J. SIMON (*Compt. rend.*, 1904, 138, 1505—1508).—A specimen

of ethyl oxalacetate which has been kept for a long time gives a violet coloration with an alkali hydroxide or with the alkali salt of a weak acid such as boric or formic. The reaction is not given by pure ethyl oxalacetate, either freshly prepared or regenerated from its copper derivative, but it is given by these specimens, at the end of a certain time, and must, therefore, be due to a product of spontaneous change. An impure specimen of the colour-giving compound was obtained from the residue left after distilling off the pure ethyl oxalacetate from a commercial sample; it is an oily liquid boiling at $210-215^{\circ}$, and the result of analysis and molecular weight determination point to it being a condensation product of two molecules of ethyl oxalacetate with the loss of one molecule of alcohol,



It is, further, more readily prepared by the action of anhydrous zinc chloride on ethyl oxalacetate. Attempts to isolate the coloured product resulting from the action of alkali hydroxides on the condensation product were unsuccessful; by treating the latter compound with dilute alkali for several days, acidifying, and then extracting with ether, an oily substance was obtained after evaporating off the ether, which develops a deep blue colour in contact with alkalis, or even water or alcohol, but no pure compound could be obtained. The author suggests that the coloured compound may be a substituted dioxyquinone, $\text{CO}_2\text{Et} \cdot \text{CH} \cdot \text{CO} \cdot \text{CO}$
 $\text{CO} \cdot \text{CO} \cdot \text{CH} \cdot \text{CO}_2\text{Et}$ formed from the colour-giving compound by the elimination of another molecule of alcohol.

M. A. W.

Stereochemical Notes [Pasteur's Method of Resolving by means of Active Compounds. Solubility of a Tartrate Compared with that of a Racemate]. WILHELM MEYERHOFFER (*Ber.*, 1904, 37, 2604—2610).—In the case of double salts, there are three temperature intervals corresponding with (1) the crystallisation from solution of the separate salts, (2) the crystallisation of the less soluble salt followed by the double salt, (3) crystallisation of the double salt only. Pasteur's method is only applicable within the limits of the first two intervals.

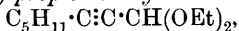
The tension of the stable or labile tartrate mixture is double that of the single tartrate. The tension of a stable racemate may be smaller, or at most twice as great, whilst that of a labile racemate is more than twice as great as that of the tartrate. In an indifferent solvent, the tension curves have the same form as the solubility curves, and the figures given in the paper are applicable to either case. T. M. L.

Preparation of Methylenecitric Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 150949).—Methylenecitric acid is best prepared by heating citric acid with chloromethyl alcohol at $130-140^{\circ}$. A yield of 80 per cent. is obtained. C. H. D.

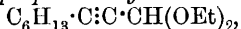
Atmospheric Formaldehyde. H. HENRIET (*Compt. rend.*, 1904, 139, 67—68. Compare this vol., i, 289).—Gautier has pointed out that 0.5 to 1 gram per 100 cubic metres is the highest proportion of

formaldehyde air can contain without ceasing to be respirable; the author therefore suggests that the large proportion (2—6 grams per 100 cubic metres) which he found experimentally may be present in the form of some compound such as methylal, from which formaldehyde is readily regenerated by the action of acids, for the amount of formaldehyde in water through which a large quantity of air has been bubbled is much increased by heating the water with dilute sulphuric or acetic acid. M. A. W.

New Method of Preparing Acetylenic Aldehydes; Action of Hydroxylamine. CHARLES MOUREU and RAYMOND DELANGE (*Compt. rend.*, 1904, 138, 1339—1341. Compare Abstr., 1901, i, 581).—The method of Bodroux (compare this vol., i, 250) and of Tschitschibabin (compare this vol., i, 221) can be applied to the preparation of the acetals of acetylenic aldehydes, $R \cdot C \equiv C \cdot CH(OEt)_2$, from which the aldehyde is obtained by hydrolysis. For this purpose, molecular proportions of magnesium ethyl bromide or iodide and the acetylenic hydrocarbon are heated to boiling for 24 hours, a slight excess of ethyl orthoformate is then added, and the heating continued for a further 24 hours; the yield of the acetal thus obtained amounts to 75 per cent. of the theoretical. *Amylpropiolaldehyde orthodiethylic ether*,

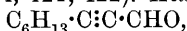


boils at 110° under 11 mm. pressure, has n_D 1.438 at 15°, and a sp. gr. 0.881 at 15°/0°. *Hexylpropiolaldehyde orthodiethylic ether*,



boils at 127° under 12 mm. pressure, has n_D 1.441 at 12°, and a sp. gr. 0.879 at 12°/0°. *Phenylpropiolaldehyde orthodiethylic ether* boils at 144—145° under 14 mm. pressure, has n_D 1.521 at 14°, and sp. gr. 0.995 at 14°/0° (compare Claisen, Abstr., 1897, i, 188).

The aldehydes obtained by hydrolysis of the first and third compounds have already been described (compare Abstr., 1901, i, 250, and Claisen, Abstr., 1898, i, 421, 422). *Hexylpropiolaldehyde*,



distils at 90—92° under 13 mm. pressure and has a sp. gr. 0.909 at 0°. The aldehydes combine with sodium hydrogen sulphite; their semicarbazones melt respectively at 90° (amyl), 78—79° (hexyl), and 137—138° (phenyl); by the action of hydroxylamine hydrochloride in the presence of sodium acetate, the oximes are not formed, but their corresponding isooxazoles (compare this vol., i, 95); 5-*amylisooxazole*,

$O \begin{array}{c} \text{N} \\ \parallel \\ \text{C} \end{array} \begin{array}{c} \text{CH} \\ \parallel \\ \text{C} \end{array} (C_5H_{11}) : \text{CH}$, boils at 87—87.5° under 14 mm. pressure and has a

sp. gr. 0.954 at 0°/0°; 5-*hexylisooxazole*, $O \begin{array}{c} \text{N} \\ \parallel \\ \text{C} \end{array} \begin{array}{c} \text{CH} \\ \parallel \\ \text{C} \end{array} (C_6H_{13}) : \text{CH}$, boils at 103—104° under 15 mm. pressure and has a sp. gr. 0.943 at 0°/0°; 5-*phenylisooxazole* melts at 18—22°, boils at 131° under 17 mm. pressure and at 254—256° (corr.) under normal pressure. M. A. W.

Chloralacetonechloroform. F. HOFMANN-LA ROCHE & Co. (D.R.-P. 151188).—Acetonechloroform and chloral hydrate are heated together for $\frac{1}{2}$ hour at 75—80° and the product dissolved in benzene.

Chloralacetonechloroform, $\text{CCl}_3 \cdot \text{CMe}_2 \cdot \text{O} \cdot \text{CH}(\text{OH}) \cdot \text{CCl}_3$, separates in asbestos-like needles, melts at 65° , and has a faint odour and taste of camphor. It sublimes when cautiously heated. Sulphuric acid hydrolyses it in the cold to chloral and acetonechloroform, potassium permanganate is only reduced on warming. The compound possesses hypnotic and local anæsthetic properties. C. H. D.

Mutual Transformation of the Two Stereoisomeric Penta-acetates of Dextrose. COENRAAD L. JUNGUIS (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 6, 779—783. Compare Abstr., 1903, i, 733).—The particular penta-acetate formed by the action of acetic anhydride on dextrose depends on the catalyser used; with dry sodium acetate, the β -form, melting at 134° , is produced (Franchimont, Herzfield), whilst with zinc chloride, the α -form, melting at 112° , is obtained (Erwin and Königs). The β - is readily converted into the α -isomeride by boiling its solution in acetic anhydride with a little zinc chloride, and the author has made a closer study of this transformation, which he finds to be caused by an intramolecular migration at the terminal asymmetric carbon atom. The transformation is not due to the addition and subsequent elimination of a molecule of the solvent, since Lobry de Bruyn has shown that by simple melting of the β -isomeride with dry zinc chloride, the α -isomeride is formed. The author has succeeded in effecting the same transformation in a chloroform solution containing sulphur trioxide.

As in the case of the two methyl glucosides, the final condition in the transformation results in a state of equilibrium. The optical activity of a solution of the β -form in acetic anhydride, together with zinc chloride, gradually increased with measurable velocity to a constant value, which was also attained in a similar manner when the α -form was employed. It is calculated that in the condition of equilibrium there exists 88 per cent. of the α - and 12 per cent. of the β -compound. The action is unimolecular; the velocity constant is 0.0095 at 35° with a concentration of 2 per cent. of zinc chloride, whilst at 45° the constant is 0.028; with 1 per cent. solutions of zinc chloride at 45° , the constant is 0.0135.

Tanret's third penta-acetate of dextrose is shown not to exist; it is simply a mixture of the α - and β -forms. If it were really a third isomeride, it might be obtained free from the others by crystallisation, and should present a definite melting point. If a mixture of the α - and β -forms is made in such proportion that the $[\alpha]_D$ is 60° , the product shows the same melting point as that given by Tanret for the third isomeride, namely, 91 — 94° . A solution saturated with both isomerides and a solution saturated with Tanret's product contain the same amount of penta-acetate, the solvent being 50 per cent. alcohol.

The two stereoisomeric methyl glucosides may be converted into the corresponding penta-acetates, and the latter into the former (Fischer and Armstrong, Abstr., 1901, i, 671). The α -glucoside corresponds with the α -penta-acetate and the β -glucoside with the β -penta-acetate.

The mutual transformation of the methylglucosides (Jungius, Abstr., 1903, i, 733) and the penta-acetates described conditions the multi-

rotation of those substances (compare Armstrong, Trans., 1903, 83, 1305).
A. McK.

Constitution of Cellulose. CHARLES F. CROSS and EDWARD J. BEVAN (*Zeit. Farb. Text.-Ind.*, 1904, 3, 197—199).—A theoretical paper unsuitable for abstraction (compare Green, *ibid.*, 97). W. A. D.

Isolation of Betaine from the Waste Liquors from the Desaccharification of Molasses by means of Strontia. KARL ANDRLIK (*Zeit. Zuckerind. Böhm.*, 1904, 28, 404—406).—After separating the amino-acids from these waste liquors by means of phosphoric acid and alcohol (see Abstr., 1903, i, 797), the alcoholic solution is treated further with syrupy phosphoric acid, by which means crystalline betaine phosphate is obtained. This phosphate is decomposed by means of milk of lime, the solution freed from lime by carbon dioxide, and the filtrate evaporated on the water-bath; on cooling, it solidifies to a crystalline mass of betaine, which is purified by crystallisation from 96 per cent. alcohol. In this way, a yield of pure betaine equal to 12 per cent. of the dry matter of the original waste liquors may be obtained.
T. H. P.

Synthesis of Polypeptides. EMIL FISCHER (*Ber.*, 1904, 37, 2486—2511. Compare Abstr., 1903, i, 465 and 799).—By making use of the method previously described, namely, the condensation of amino-acids with halogen-substituted acid chlorides, a large number of polypeptides of all classes have been prepared. *i-Glycylalanine*, $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, prepared by heating chloroacetylalanine with ammonia, melts and decomposes at 227° (corr.) and forms a carbethoxy-derivative identical with that previously described. The intermediate *chloroacetylalanine* crystallises in colourless, four-sided, oblique plates melting at $125\text{--}127^\circ$ (corr.). *α -Bromoisohexoyl-leucine*, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CHMe}_2$, prepared by the interaction of leucine and bromoisohexoyl chloride, crystallises in oblique, four-sided plates, which melt to a clear liquid at $188\text{--}189^\circ$ (corr.) and on heating with ammonia form leucyl-leucine (*loc. cit.*). *Chloroacetyl-l-tyrosine* crystallises in prisms melting at $155\text{--}156^\circ$ (corr.) and shows Millon's reaction. The corresponding ester, prepared by the action of chloroacetyl chloride on tyrosine ethyl ester, crystallises in needles melting at $87\text{--}88^\circ$ (corr.). Both compounds, when heated at 100° with aqueous ammonia, form *glycyl-l-tyrosine*.

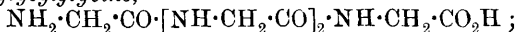
$\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, which sinters at 125° and melts at 165° . Trypsin at 36° hydrolyses it, separating tyrosine. The *ethyl* ester melting at 245° (corr.) has been obtained crystalline. *α -Bromoisohexoyl-l-tyrosine*, which can be prepared either from tyrosine itself or from its ethyl ester, crystallises from water in globular aggregates of needles and melts at $139\text{--}140^\circ$ (corr.). It and the following compound are possibly mixtures of two stereoisomerides. On heating with ammonia, *leucyl-l-tyrosine* is formed, which shows Millon's reaction and dissolves copper oxide with a deep blue coloration, but has as yet only been obtained in an amorphous condition.

Leucyltyrosine anhydride, $C_4H_9 \cdot CH \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} CH \cdot CH_2 \cdot C_6H_4 \cdot OH$,

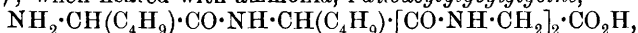
which is obtained as a by-product and is best prepared by heating the oily ethyl ester from α -bromoisohexoyltyrosine with alcoholic ammonia, crystallises in slender needles and melts and decomposes at 310° (corr.).

The preparation of diglycylglycine (*loc. cit.*, 799) is improved by preparing chloroacetylglycylglycine directly from glycylglycine hydrochloride and chloroacetyl chloride and subjecting this compound to the action of ammonia in the cold instead of at 100° .

Chloroacetyldiglycylglycine, which melts and decomposes at 224° (corr.), yields, on heating with aqueous ammonia at 100° , the tetrapeptide, *triglycylglycine*,



this colours at 220° and becomes quite dark at 270° without melting; it shows a biuret coloration in alkaline solution and is soluble in about 4 parts of hot water. The hydrochloride of the ethyl ester melts at 212 — 214° (Curtius, *Abstr.*, 1902, i, 844, gives 192 — 193°) and the benzoyl derivative at 235° (Curtius, *loc. cit.*). α -Bromoisohexoyl-leucylglycylglycine, prepared by the interaction of leucylglycylglycine and α -bromoisohexoyl chloride, sinters at 152° and melts at 161 — 162° (corr.); when heated with ammonia, *i*-dileucylglycylglycine,



is formed. This crystallises in microscopic needles aggregated in bunches and melts about 250° .

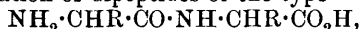
Chloroacetyltriglycylglycine becomes yellow at 230° and melts and decomposes at 256° (corr.). On heating with ammonia, the pentapeptide *tetraglycylglycine*, $NH_2 \cdot CH_2 \cdot CO \cdot [NH \cdot CH_2 \cdot CO]_3 \cdot NH \cdot CH_2 \cdot CO_2H$, is formed; this is sparingly soluble in water; on heating, it becomes coloured at 246° (corr.) and decomposes at higher temperatures.

$\alpha\beta$ -Dibromopropionyl chloride (Moureu, *Abstr.*, 1903, i, 312) is conveniently prepared by the interaction of $\alpha\beta$ -dibromopropionic acid with an equal weight of phosphorous pentachloride; it boils at 71 — 73° under 12 mm. pressure and reacts readily with the peptides.

$\alpha\beta$ -Dibromopropionylglycine crystallises in needles, melting at 147 — 148° (corr.) and decomposing at 170° . $\alpha\beta$ -Dibromopropionylglycylglycine forms microscopic, obliquely cut prisms melting at 184° (corr.). The *ethyl* ester prepared from glycylglycine ester crystallises in prisms, which sinter at 145° and melt at 151 — 152° (corr.). *Bromoacrylglycylglycine*, $C_2H_2Br \cdot CO \cdot NH \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$, prepared by the action of cold sodium hydroxide on the preceding compound, crystallises in prisms melting at 202° (corr.). The possibility of the formation of stereoisomerides by these syntheses is also discussed.

E. F. A.

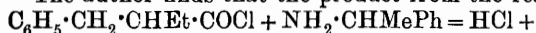
Evidence for the Possibility of Resolving an Optically Active Compound without actually Resolving it and without the Aid of Optically Active Substances. ERNST MOHR (*Ber.*, 1904, 37, 2702—2704).—E. Fischer has indicated (preceding abstract) that, in the preparation of dipeptides of the type



a mixture of two stereoisomeric racemic products may be obtained in different amounts, starting with inactive material.

Since, theoretically, in the general reaction $\text{CHXY} \cdot \text{COCl} + \text{NH}_2 \cdot \text{CHUV} = \text{HCl} + \text{CHXY} \cdot \text{CO} \cdot \text{NH} \cdot \text{CHUV}$ (where the asymmetric carbon atoms are represented by *), a mixture of two stereoisomeric racemic acid amides may be formed, reactions of this nature may be of use in settling whether a given acid chloride or amine is racemic or not.

The author finds that the product from the reaction

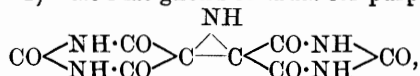


$\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CHEt} \cdot \text{CO} \cdot \text{NH} \cdot \text{CHMePh}$ is a mixture melting at $60-80^\circ$, which, by systematic crystallisation from light petroleum, may be separated into two isomeric substances. The more sparingly soluble constituent separates in slender, white needles, softens at 109° , and melts at 112° ; the isomeride forms silky needles, softens at 75° , and melts at $85-87^\circ$. The latter is present in the mixture in larger quantity than the former.

In accordance with theory, the compounds

$\text{CH}_2\text{Ph} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CHMePh}$ (m. p. 89°) and $\text{CH}_2\text{Ph} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2\text{Ph}$ (m. p. 85°) exist in one modification only. A. McK.

Constitution of Purpuric Acid and Murexide. RICHARD MÖHLAU (*Ber.*, 1904, 37, 2686—2691).—Piloty points out (*Annalen*, 1904, 333, Heft 1) that Matignon's formula for purpuric acid,

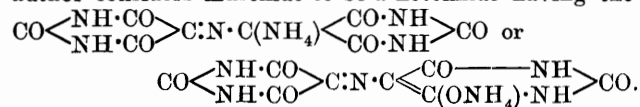


which represents this acid as an imide of alloxantin, is in accordance neither with its instability nor with the intense coloration of its salts.

The formula $\text{CO} \begin{array}{c} \diagup \text{NH} \cdot \text{CO} \\ \diagdown \text{NH} \cdot \text{CO} \end{array} \text{C} : \text{N} \cdot \text{CH} \begin{array}{c} \diagdown \text{CO} \cdot \text{NH} \\ \diagup \text{CO} \cdot \text{NH} \end{array} \text{CO}$ is more probably correct, since murexide is decomposed by boiling its aqueous solution into alloxan and uramil, a little alloxantin being also formed. The author further gives evidence for the existence of purpuric acid in the free state, and shows that the acid itself splits up into alloxan and uramil.

Dibarbityrylmethylamine, prepared by boiling an aqueous solution of alloxantin (or dialuric acid) with methylamine hydrochloride, separates from water in transparent, rhombic crystals, which decompose at 240° . By oxidation of this compound, however, it was not found possible to prepare an *N*-substituted murexide.

Piloty's views as to the constitution of murexide are discussed. The author considers murexide to be a ketoimide having the constitution



A. McK.

Preparation of Hydrogen Cyanide. HERMANN CHARLES WOLTERECK (D.R.-P. 151130).—Kuhlmann's synthesis of hydrogen cyanide (1841) by passing ammonia and a volatile hydrocarbon over a heated catalytic substance may be employed technically if care is taken to dry the gases thoroughly and to ensure the presence of free hydrogen. The temperature required is higher the more complex the carbon compound employed. A mixture of 1 part of ammonia and 2 parts of water-gas (carbon monoxide and hydrogen) may be used with advantage. The mixed dry gases are passed over platinised pumice heated to bright redness, and the hydrogen cyanide formed is absorbed in water or solutions of alkali hydroxides. C. H. D.

[**Preparation of Cyanogen Compounds.**] HERMANN MEHNER (D.R.-P. 151644).—The preparation of cyanides from alkalis, carbon, and atmospheric nitrogen in a furnace offers great difficulties. An improved arrangement is described, in which a cupola furnace containing coal or coke is used, air being forced through the burning mass. Water-glass or an alkaline or alkaline earthy slag is added at the top of the furnace, and, becoming strongly heated, descends to the lower part, which acts as a Siemens' producer and contains a reducing atmosphere. Here cyanogen compounds are formed, and escape, mixed with carbon monoxide and some nitrogen, through an outlet near the base of the furnace. The products of combustion in the upper (oxidising) portion escape at the top. The hot slag is returned to the furnace, loss of alkali being made good by the addition of sodium carbonate. Metallic iron, formed by reduction of the ash of the coke, accumulates in the slag and greatly facilitates the reaction (compare Täuber, Abstr., 1901, ii, 107; 1903, i, 328). C. H. D.

A Constituent of Gas Purification Residues: Iron Carbonylferrocyanide. MAX STOECKER (*Chem. Centr.*, 1904, i, 1406; from *J. f. Gasbel.*, 47, 338—342. Compare Abstr., 1904, i, 147).—The residues obtained in the purification of coal gas contain only an extremely small quantity of iron carbonylferrocyanide, and attempts to isolate this compound failed. Large quantities have been prepared, however, from the violet filtrate obtained after precipitating the potassium ferrocyanide with ferric chloride. The iron carbonylferrocyanide was converted into the potassium salt by four different methods. Potassium carbonylferrocyanide, $K_3FeCO(CN)_5$, forms small, faintly yellow to colourless crystals which contain varying amounts of water of crystallisation. Iron carbonylferrocyanide, $Fe'''Fe''CO(CN)_5$, prepared by the action of an excess of ferric chloride on the corresponding potassium compound, resembles indigo in appearance and contains about 4 per cent. of water of crystallisation. The usual methods of estimating the quantity of Prussian blue in gas residues, such as those of Knublauch, Drehschmidt, &c., give results which include the amount of the violet carbonyl compound which is also present. Owing to the very small proportion of the latter, however, and the ease with which it is converted into Prussian blue, the error is of no practical importance. The carbonyl compounds are almost entirely converted into Prussian blue in the purification process itself;

in a residue containing 10 per cent. of Prussian blue, there would only be about 0.1 per cent. of the pure violet compound.

Iron carbonylferrocyanide is prepared from the last mother liquor obtained in the preparation of potassium ferrocyanide. The liquor, which contains potassium carbonylferrocyanide together with a considerable quantity of potassium ferrocyanide and other salts, is precipitated with ferric chloride, the precipitate decomposed by alkali by Lindemann's method, the ferric hydroxide removed, the filtrate evaporated to dryness, and the residue melted with powdered iron.

E. W. W.

Dibenzoyldiazomethane. HEINRICH WIELAND and SIEGFRIED BLOCH (*Ber.*, 1904, 37, 2524—2528. Compare this vol., i, 596).—*Dibenzoyldiazomethane*, prepared from dibenzoylmethane in cold ethereal solution by the action of nitrous fumes and isolated under special precautions, crystallises from 96 per cent. alcohol in yellow, rhombic plates melting and decomposing violently at 114°; it shows all the reactions of aliphatic diazo-compounds. *Anilindibenzoylmethane*, $\text{CHBz}_2\cdot\text{NHPh}$, prepared from it by heating with aniline, crystallises in colourless needles melting at 168—169°. E. F. A.

Alkyl Derivatives of Thallium. RICHARD J. MEYER and ALFRED BERTHEIM (*Ber.*, 1904, 37, 2051—2062).—A new method is described of preparing dialkylthallium compounds from thallium chloride by means of magnesium alkyl haloids.

Thalliumdimethyl bromide, TlMe_2Br , crystallises in white, silvery flakes and decomposes with liberation of gas above 275°.

Thalliumdimethyl iodide, TlMe_2I , precipitated by potassium iodide from the mother liquors of the bromide, crystallises from dilute ammonia in silver-white flakes and decomposes at 264—266°.

Thalliumdimethylthiol, TlMe_2SH , decomposes with incandescence when heated or when dropped into fuming nitric acid.

Thalliumdimethyl chloride, TlMe_2Cl , separates in glistening, white, shimmering scales and decomposes above 280°.

Thalliumdiethyl chloride, TlEt_2Cl , resembles the preceding compound, but is less soluble and decomposes at 205—206°. The iodide, TlEt_2I , crystallises from pyridine and decomposes at 185—187°. The bromide, TlEt_2Br , decomposes above 270°. The thiol, TlEt_2SH , resembles the methyl derivative. The hydroxide, TlEt_2OH , prepared by the action of silver oxide on the iodide, dissolves readily in water and alcohol, is a strong alkali, rapidly absorbs carbon dioxide, and precipitates metallic hydroxides from their salts; unlike its salts, it melts at 127—128° and decomposes at a higher temperature. The carbonate, $(\text{TlEt}_2)_2\text{CO}_3$, crystallises from water in glistening needles, decomposes at 204°, and has all the properties that Hartwig (*Abstr.*, 1875, 1002) ascribed to the base. The hydrogen carbonate, $\text{TlEt}_2\cdot\text{HCO}_3$, is precipitated as a white, feebly alkaline, crystalline powder when carbon dioxide is passed into a solution of the carbonate and alcohol then added.

Thalliumdipropyl chloride, TlPr_2Cl , crystallises from dilute ammonia in silvery flakes and decomposes at 198—202°. The iodide decom-

poses at 183—185°. The *nitrate* is sparingly soluble and crystallises exceptionally well. The *thiol* resembles those just described. The *hydroxide* was obtained only as an oil.

Thalliumdiphenyl bromide, $\text{TI}(\text{Ph})_2\text{Br}$, crystallises from alcoholic ammonia or from pyridine in minute, white needles and decomposes at 270°.

In all these compounds, the tervalent character of the thallium is very strongly marked. T. M. L.

Action of Dilute Nitric Acid on Haloid Compounds. II. MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 537—539).—The action of dilute nitric acid on bromo-*o*-xylene yields:

(1) 5-Bromo-*o*-nitro-*o*-xylene, $\text{C}_6\text{H}_3\text{MeBr}\cdot\text{CH}_2\cdot\text{NO}_2$, which melts at 65°; its salts, when mixed with ferric chloride and ether, give the reaction for nitro-compounds.

(2) 5-Bromo-*o*-toluic acid, $\text{C}_6\text{H}_3\text{MeBr}\cdot\text{CO}_2\text{H}$, which may also be obtained by oxidising the compound (1) by means of potassium permanganate and which melts at 175°.

(3) A liquid nitro-compound.

With bromo-*p*-xylene, dilute nitric acid gives a liquid and a solid nitro-compound, the latter melting at 198—200°. T. H. P.

Nitration of *p*-Tolylnitromethane [*o*-Nitro-*p*-xylene]. MICHAEL I. KONOWALOFF and SENTSHIKOVSKY (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 462—465).—When a hydrogen atom in the benzene nucleus is replaced by the residue, $\cdot\text{CH}_2\cdot\text{NO}_2$, the latter influences a nitro-group entering the nucleus in the same way as do the groups NO_2 , CHO , CO_2H ; that is, the nitro-group will enter in the meta-position to the $\cdot\text{CH}_2\cdot\text{NO}_2$, if that position is unoccupied, or in the ortho-position if the meta-position is occupied, and the nitration is carried out in the cold with nitric acid of sp. gr. 1.48. T. H. P.

Iodoso-, Iodoxy-, and Iodinium-compounds of 4-Iodo-1-methyl-3-ethylbenzene. CONRAD WILLGERODT and LOUIS BRANDT (*J. pr. Chem.*, 1904, [ii], 69, 433—448).—4-Amino-1-methyl-3-ethylbenzene, obtained by heating ethyl alcohol and *p*-toluidine with zinc chloride at 280°, distils at 218—220°. The *sulphate*,

$(\text{C}_6\text{H}_3\text{MeEt}\cdot\text{NH}_2)_2\cdot\text{H}_2\text{SO}_4$, crystallises in large leaflets and melts at 241°. When the base is diazotised and warmed with absolute alcohol, a red oil is obtained. This boils at 160°, and, when oxidised successively with nitric acid and with potassium permanganate in alkaline solution, yields *isophthalic acid*.

The action of potassium iodide on diazotised 4-amino-1-methyl-3-ethylbenzene leads to the formation of 4-iodo-1-methyl-3-ethylbenzene, which crystallises in glistening leaflets, melts at 34°, and boils at 222—225°. When acted on by chlorine in glacial acetic acid solution, it yields the *iodochloride*, $\text{C}_6\text{H}_3\text{MeEt}\cdot\text{ICl}_2$, which crystallises in long needles and melts at 108°.

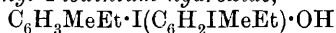
4-Iodoso-1-methyl-3-ethylbenzene, $\text{C}_6\text{H}_3\text{MeEt}\cdot\text{IO}$, is amorphous and explodes at 209°. The *iododiacetate* crystallises in clear, transparent

prisms. The basic *sulphate*, $\text{SO}_4[\text{I}(\text{OH})\cdot\text{C}_6\text{H}_3\text{MeEt}]_2$, crystallises in prisms.

4-Iodoxy-1-methyl-3-ethylbenzene, $\text{C}_6\text{H}_3\text{MeEt}\cdot\text{IO}_2$, prepared by the action of sodium hypochlorite on the iodoso-compound, crystallises in white leaflets and explodes at 229° .

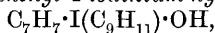
Di-1-methyl-3-ethylphenyliodinium hydroxide, $\text{I}(\text{C}_6\text{H}_3\text{MeEt})_2\cdot\text{OH}$, prepared from the iodoso- and iodoxy-compounds, is obtained as a strongly alkaline aqueous solution. The *chloride* melts at 120° ; the *bromide* melts at 162° ; the *iodide* is a yellow, amorphous substance; the *mercurichloride* crystallises in transparent plates and melts at 197° ; the orange-coloured *platinichloride* melts and decomposes at 166° .

The action of cold concentrated sulphuric acid on 4-iodoso-1-methyl-3-ethylbenzene leads to the formation of 1-methyl-3-ethylphenyl-(1)-iodo-1'-methyl-3'-ethylphenyl-4-iodinium hydroxide,



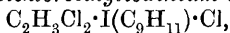
(Hartmann and Meyer, *Abstr.*, 1894, i, 242), which is obtained in a strongly alkaline aqueous solution. The *chloride* is a white, amorphous powder and melts and decomposes at 157° ; the *bromide* is amorphous and melts at 151° ; the *iodide* is obtained as a yellow, amorphous precipitate and melts and decomposes at 145° ; the *platinichloride* is a yellow powder and melts at 173° .

o-Tolyl-1-methyl-3-ethylphenyl-4-iodinium hydroxide,



is obtained from *o*-iodoxytoluene and 4-iodoso-1-methyl-3-ethylbenzene as an alkaline solution in water. The *chloride* melts at 177° ; the *bromide* is obtained as a white, amorphous precipitate and melts at 175° ; the *iodide* is a yellow, amorphous powder which melts at 168° ; the *platinichloride* is orange-coloured and melts at 176° ; the *dichromate* is obtained as a red precipitate.

1-Methyl-3-ethylphenyldichloroethyliodinium chloride,



prepared by the action of silver chloride and silver acetylide on methylethylphenyl iodochloride (*Abstr.*, 1895, i, 635), is a white, amorphous powder, which melts and decomposes at 171° ; the *bromide* is a white, amorphous powder and melts and decomposes at 150° ; the yellow, amorphous *iodide* melts at 96° ; the orange-coloured *platinichloride* melts at 132° ; the *mercurichloride* melts at 121° ; the *dichromate* forms a yellow, flocculent precipitate. G. Y.

Triphenylmethyl. IX. MOSES GOMBERG and L. H. CONE (*Ber.*, 1904, 37, 2033—2051. Compare *Abstr.*, 1901, i, 77, 319, 638, 690; 1902, i, 534, 600, 754; 1903, i, 81, 244).—The substance was prepared by the action of zinc on the chloride in a special form of apparatus, in which the whole operation of preparing the crystalline compound was effected in an atmosphere of carbon dioxide. The purified compound is quite insoluble in light petroleum, ethyl chloroacetate, and ethyl chlorocarbonate, and only sparingly soluble in chlorobenzene, benzyl chloride, and hot ethyl and methyl alcohols. It is moderately soluble in carbon tetrachloride and in toluene (from which magnificent crystals separate containing toluene), more so on heating or in ethyl iodide and ethylene bromide, and very readily in hot or cold chloroform and

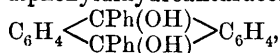
carbon disulphide. The purest material melted at 145—147°, but not sharply. Distillation under reduced pressure gave triphenylmethane. Molecular weight determinations in an atmosphere of nitrogen gave, as a mean of 12 series of observations in benzene, naphthalene, nitrobenzene, dimethylaniline, *p*-bromotoluene, and phenol, the mean value $M = 477$, whilst $(C_6H_5)_3C$ requires $M = 243$, so that the substance is clearly dimolecular. This conclusion was confirmed by the observation that the depression of the freezing point of a solution of the chloride in nitrobenzene gradually decreased from 0.567 to 0.311, and from 1.197 to 0.647 in two series of experiments in which the chloride was converted into triphenylmethyl by the action of silver. The figures quoted correspond with a rise of molecular weight in the ratios 279 to 509 and 278 to 514.

Walden's observation that solutions of triphenylmethyl in sulphur dioxide have a marked conductivity was confirmed with freshly prepared and highly purified material. The molecular conductivity ($M = 486$) rose from $\mu = 16.48$ when $v = 24$ to $\mu = 39.6$ when $\mu = 2138$, and similar values were obtained in three other series of observations.

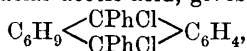
Triphenylmethyl is shown by this series of observations to be a dimolecular compound, but is not identical with hexaphenylethane. The nature of the isomerism is still somewhat obscure, but the author maintains the view that the compound is essentially a derivative of tervalent carbon, CPh_3- , although in solution there is a tendency to form a loose bimolecular compound, which may be compared to the loose polymerides of water, nitriles, and organic acids. T. M. L.

Bistriphenylmethyl and Hexaphenylethane. DANIEL VORLÄNDER (*Ber.*, 1904, 37, 2397. Compare Gomberg, this vol., i, 489).—Bistriphenylmethyl and hexaphenylethane form an example of additive isomerism. The properties of these two substances are expressed by the formulæ $(CPh_3)(CPh_3)$ for bistriphenylmethyl and $CPh_3 \cdot CPh_3$ for hexaphenylethane. G. Y.

s-9:10-Diphenylanthracene and 9:10-Diphenyldihydroanthracene. ALBIN HALLER and ALFRED GUYOT (*Compt. rend.*, 1904, 138, 1251—1254. Compare this vol., i, 83, 314, 346).—Phenyloxanthranol, $C_6H_9 \begin{smallmatrix} \text{CPh(OH)} \\ \text{CO} \end{smallmatrix} C_6H_4$, melting at 207°, is obtained when an ethereal solution of magnesium phenyl bromide is slowly added to a suspension of anthraquinone in anhydrous ether. By further action of the magnesium compound on phenyloxanthranol, 9:10-dihydroxy-9:10-diphenyldihydroanthracene,

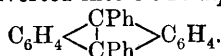


is obtained. The *monomethyl ether* forms colourless crystals melting at 274°. The diol, when treated with alcoholic hydrogen chloride in boiling solution in glacial acetic acid, gives the *dichloride*,



melting at 178°. The chloride acts as an energetic oxidising agent, and

by loss of chlorine is converted into 9 : 10-*diphenylanthracene*,



The hydrocarbon is most readily obtained by treatment of the dichloride with zinc or potassium iodide in acetic acid solution ; it separates from carbon disulphide in yellow crystals melting at 240°, and in most solvents it exhibits fluorescence.

9 : 10-*Diphenyldihydroanthracene*, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CHPh} \\ | \\ \diagdown \text{CHPh} \end{array} \text{C}_6\text{H}_4$, obtained by the prolonged action of sodium amalgam on 9 : 10-diphenylanthracene suspended in alcohol, dissolves readily in toluene and is precipitated by alcohol in slender needles melting at 218°. On heating, it loses hydrogen ; its solutions do not fluoresce. H. M. D.

Syntheses in the Anthracene Series. II. 9 : 9 : 10-Triphenyldihydroanthracene and Derivatives. ALBIN HALLER and ALFRED GUYOT (*Compt. rend.*, 1904, 139, 9—13. Compare Abstr., 1901, i, 350 ; 1903, i, 200, 348 ; this vol., i, 83, 314, 346).—10-*Hydroxy*-

9 : 9 : 10-*triphenyldihydroanthracene*, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CPh}_2 \\ | \\ \diagdown \text{CPh(OH)} \end{array} \text{C}_6\text{H}_4$, obtained quantitatively by means of the Grignard synthesis from diphenylanthrone and magnesium phenyl bromide, forms colourless, voluminous crystals containing ether (1 mol.), which it loses at 120°, melts at 200°, resembles triphenylcarbinol in giving an orange-red coloration with sulphuric acid, in forming condensation products with phenol (compare Baeyer and Villiger, Abstr., 1902, i, 769) and with aniline (compare Ullmann and Münzhuber, Abstr., 1903, i, 245), and in being readily etherified by boiling with alcohol and a few drops of hydrochloric acid ; the *methyl ether* forms white, pearly plates melting at 218°, and the *ethyl ether* forms white needles melting at about 250°.

9 : 9 : 10-*Triphenyldihydroanthracene*, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CPh}_2 \\ | \\ \diagdown \text{CHPh} \end{array} \text{C}_6\text{H}_4$, obtained by reducing the hydroxy-compound by means of zinc and acetic acid, forms white crystals melting at about 220°, and is sparingly soluble in the ordinary solvents. A second synthesis of this hydrocarbon is effected by means of the Grignard reaction from *methyl triphenylmethane-o-carboxylate*, which is prepared by the action of methyl sulphate on an alkaline solution of triphenyl methane-*o*-carboxylic acid, forms white prisms melting at 98°, and condenses with magnesium phenyl bromide to form the compound $\text{OMe} \cdot \text{CPh}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHPh}_2$, which melts at 215° and readily loses a mol. of methyl alcohol on treatment with concentrated sulphuric or hydrochloric acid to form 9 : 9 : 10-triphenyldihydroanthracene.

Attempts to effect a further synthesis of this hydrocarbon from methyl phthalate or methyl benzoylbenzoate and magnesium phenyl bromide were unsuccessful. M. A. W.

Direct Reduction of the Homologues of Aniline. PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1904, 138, 1257—1259).—The authors have previously shown (this vol., i, 305) that, under the influence of hot, finely-divided nickel, aniline is reduced

to cyclohexylamine with secondary formation of dicyclohexylamine and cyclohexylaniline. The homologues of aniline have now been investigated. Methyl- and ethyl-anilines give respectively cyclohexylmethylamine, $C_6H_{11} \cdot NHMe$, boiling at 145° , and cyclohexylethylamine boiling at 164° (corr.), having a sp. gr. 0.868 at $0^\circ/0^\circ$. The odour of these liquids strongly resembles that of methyl- and ethyl-amines. With phenylcarbimide, the ethyl compound yields phenylcyclohexylethylcarbamide, $NHPh \cdot CO \cdot NEt \cdot C_6H_{11}$, which crystallises in colourless, rhombic laminæ and melts at 125° (corr.); the corresponding thiocarbamide melts at 126° . cyclohexyldimethylamine, boiling at 165° (corr.) and having a sp. gr. 0.876 at $0^\circ/0^\circ$, and the corresponding diethyl compound, boiling at 193° (corr.) and having a sp. gr. 0.872 at $0^\circ/0^\circ$, are similarly formed from dimethyl- and diethyl-aniline. The secondary actions observed in the case of aniline are not met with in the reduction of the above homologues. On the other hand, *m*-toluidine behaves quite similarly to aniline and gives rise to three products, one of which is 1:3-methylcyclohexylamine, which boils at 150° , and the other two appear to be dimethylcyclohexylamine, boiling at 145° under 20 mm. pressure, and methylcyclohexylaniline, boiling at 175° under 20 mm. pressure.

H. M. D.

Conditions of the Interaction between Aniline Vapour and Aluminium Chlorate Solution. DMITRI K. DOBROSERDOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 483—485).—Filter paper soaked in aluminium chlorate solution and left in the laboratory in presence of aniline vapour gradually assumes an intense blue colour, which slowly changes to a dirty green. This phenomenon is due to oxidation of the aniline, the final product of which is known as nigraniline, which is an extremely stable dye. The blue colour obtained is that of an intermediate, basic, oxidation product which, in the form of salts of a green colour, is known as emeraldine. Glass smeared with nitric acid also becomes coloured in presence of aniline vapour, the final product being emeraldine.

T. H. P.

Iodine Derivatives of *m*-Nitroaniline. P. BRENANS (*Compt. rend.*, 1904, 138, 1503—1505; 139, 63—65. Compare Abstr., 1901, i, 322, 643; 1902, i, 280, 673; 1903, i, 336; this vol., i, 157).—By the action of iodine chloride on *m*-nitroaniline in acetic acid solution, three iodine derivatives were obtained: I. 6-iodo-3-nitroaniline crystallises from alcohol in yellow needles melting at 160° (corr.), is soluble in all ordinary organic solvents except light petroleum, and on diazotising and boiling with alcohol yields 1-iodo-4-nitrobenzene melting at 171.5° and identical with the compound obtained by substituting iodine for the NH_2 group in *p*-nitroaniline. II. 2:5-Di-iodo-3-nitroaniline crystallises from a mixture of chloroform and light petroleum in large, yellow prisms melting at 125° (corr.), is very soluble in the ordinary solvents with the exception of light petroleum, and on diazotising with amyl nitrite and subsequent boiling, yields 1:3-di-iodo-2-nitrobenzene, which crystallises from a mixture of chloroform and light petroleum in large prisms melting at 114° (corr.), soluble in all the ordinary solvents except light petroleum, and is reduced by ferrous sulphate

and ammonia to 1:6-*di-iodoaniline*, which crystallises in colourless needles melting at 122° (corr.), is soluble in the ordinary solvents, forms a *diacetyl* derivative crystallising in colourless needles melting at 147° (corr.), and on diazotising and boiling with water yields 1:6-di-iodophenol, melting at 68° and identical with the compound prepared by Schaal (compare Abstr., 1883, 1109). III. 2:6-Di-iodo-3-nitroaniline, identical with the compound prepared by Michael and Norton (compare Abstr., 1878, 406), crystallises in orange-yellow needles melting at 149° (corr.), soluble in all the ordinary organic solvents except light petroleum, and on diazotising and boiling with alcohol yields 2:4-*di-iodonitrobenzene*, which forms yellow crystals, melts at 101°, resembles the preceding compound in solubility, and is reduced by stannous chloride to 2:4-di-iodoaniline, identical with Michael's compound (compare *loc. cit.*), and forming a *di-acetyl* derivative which crystallises in thin, colourless needles from alcohol, melts at 93°, and is very soluble in alcohol and acetic acid. The identity of the di-iodoaniline was further confirmed by converting it by the ordinary processes into the corresponding phenol. The compound thus obtained melted at 72° and was identical with Schaal's 2:4-di-iodophenol (Abstr., 1883, 1109).

Koerner has described a 2:4-di-iodonitrobenzene melting at 168.4°, and obtained by heating 1:3-di-iodobenzene with fuming nitric acid (Abstr., 1876, i, 222); the author has repeated the experiment and finds that the compound melting at 168° obtained under these conditions is a *di-iododinitrobenzene*; if, however, 1:3-di-iodobenzene is heated at 80° with a mixture of acetic acid and fuming nitric acid, 2:4-di-iodonitrobenzene is the only product. M. A. W.

New Method of Preparing Anilides. F. BODROUX (*Compt. rend.*, 1904, 138, 1427—1429).—The organomagnesium compounds prepared by Meunier (compare Abstr., 1903, i, 544) from a primary amine and a magnesium alkyl haloid condense readily with the esters of monobasic acids to yield the corresponding mono-substituted derivative of the acid amide, according to the equations: $2\text{NHR} \cdot \text{MgI} + \text{R}'\text{CO}_2\text{R}'' = \text{MgI} \cdot \text{OR}'' + \text{R}'\text{C}(\text{NHR})_2 \cdot \text{O} \cdot \text{MgI}$; $\text{R}'\text{C}(\text{NHR})_2 \cdot \text{OMgI} + \text{HCl} = \text{NH}_2\text{R} + \text{MgClI} + \text{R}'\text{CO} \cdot \text{NHR}$. The ester is added to an ethereal solution of the compound $\text{NHR} \cdot \text{MgI}$, and the resulting compound decomposed by dilute hydrochloric acid; the yield is almost quantitative. The following substituted amides were thus prepared: formanilide, formo- β -naphthalide, acetanilide, aceto-*p*-toluidide; aceto- β -naphthalide; propionanilide; propiono-*o*-toluidide; propiono-*p*-toluidide; benzanilide; benzo-*o*-toluidide; salicylanilide, and salicyl-*p*-toluidide. M. A. W.

5-Nitro-2-aminotoluene- ω -sulphonic Acid. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 150366).—*o*-Chlorotoluene- ω -sulphonic acid, prepared by boiling *o*-chlorobenzyl chloride with sodium hydrogen sulphite, may be nitrated in sulphuric acid solution, forming 2-chloro-5-nitrotoluene- ω -sulphonic acid, the sodium salt of which forms yellow, sparingly soluble needles. When heated with ammonia at 150°, yellow crystals of ammonium 5-nitro-2-aminotoluene- ω -sulphonate are formed. The chlorine atom may also be replaced by amino-residues by heating with amines. The sodium salts of 5-nitro-2-anilino-

toluene-o-sulphonic acid and of the corresponding *o*- and *p*-*toluidino-acids* are described.
C. H. D.

Aromatic Derivatives of Oxamide and Carbanilide. PAUL CAMILL TAUSSIG (*Monatsh.*, 1904, 25, 375—390).—When a mixture of oxanilide and mercuric oxide is heated at 350° in a slow current of carbon dioxide, 20—25 per cent. of the oxanilide is converted into carbanilide. With oxalyl-*o*-toluidide, the reaction takes place at a lower temperature, and a 40—50 per cent. yield of *s*-di-*o*-tolylcarbamide is obtained.

The action of bromine (2 mols.) on oxalyl-*o*-toluidide (1 mol.) in hot saturated glacial acetic acid solution leads to the formation of *di-m-bromo-o-oxalyltoluidide*, $C_2O_2(NH \cdot C_7H_6Br)_2$, which crystallises in white, glistening needles, melts at 254—255°, and is soluble in benzene, toluene, or boiling aniline or nitrobenzene. When hydrolysed with alcoholic potassium hydroxide, it yields *m*-bromo-*o*-toluidine (Wroblewski, *Annalen*, 1873, 168, 162). The action of bromine on excess of oxalyl-*o*-toluidide leads to the formation of *m-bromo-o-oxalyltoluidide*, $C_7H_7 \cdot NH \cdot C_2O_2 \cdot NH \cdot C_7H_6Br$, which crystallises in matted, slender needles, melts at 186°, and is soluble in alcohol. Both bromine compounds distil without decomposition. 2:2':3:3'-Tetramethylcarbanilide is obtained by heating *oxalyl-as-xylidide* with mercuric oxide. Di-*m*-tolylcarbamide, formed by heating *m*-toluidine with carbamide or by distilling oxalyl-*m*-toluidide with mercuric oxide, melts at 221°.

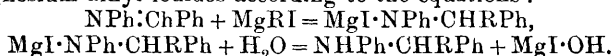
o-Tolidine oxalate, $(C_7H_8N)_2, C_2H_2O_4$, formed from *o*-tolidine and oxalic acid in alcoholic solution, crystallises from boiling water in leaflets and melts and decomposes at 215°.

Oxalyl-o-tolidine, $\begin{array}{c} C_7H_6 \cdot NH \cdot CO \\ | \\ C_7H_6 \cdot NH \cdot CO \end{array}$, prepared by boiling *o*-tolidine with ethyl oxalate, crystallises from alcohol, acetone, or glacial acetic acid in white, flocculent aggregates, melts at 335°, and is hydrolysed to *o*-tolidine and oxalic acid by aqueous alkali hydroxide.

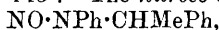
Carbonyl-o-tolidine, $\begin{array}{c} C_7H_6 \cdot NH \\ | \\ C_7H_6 \cdot NH \end{array} > CO$, is formed when an alcoholic solution of *o*-tolidine and carbamide is evaporated to dryness and the residue heated at 125—130°, or when oxalyl-*o*-tolidide is distilled with mercuric oxide. It crystallises from warm concentrated sulphuric acid in small, transparent crystals, melts at 355—358° (370—373°, corr.), and is very stable.

Di-*m*-nitrocarbanilide is formed when crude di-*m*-nitro-oxanilide, prepared by heating *m*-nitroaniline with crystalline oxalic acid, is distilled with mercuric oxide.
G. Y.

Behaviour of Magnesium Organo-compounds towards Benzylideneaniline. MAX BUSCH (*Ber.*, 1904, 37, 2691—2694).—Magnesium alkyl haloids interact with alkylidene bases, addition taking place at the $\cdot CH:N$ grouping; thus, benzylideneaniline acts on magnesium alkyl iodides according to the equations:



α-Anilinoethylbenzene nitrate, prepared by adding dilute nitric acid to the product obtained from magnesium methyl iodide (1 mol.) and benzylideneaniline (1 mol.), separates in glistening needles and melts at 162—163°. The free *base*, $\text{NPh}\cdot\text{CHMePh}$, is a viscid oil which boils at 183° under 20 mm. pressure; the *hydrochloride* crystallises in needles and melts at 184—185°; the *sulphate* crystallises in hexagonal, monoclinic plates and melts at 142—143°. The *nitroso-derivative*,



is a brownish-yellow oil; it forms a salt with an alcoholic solution of hydrogen chloride, which yields acetophenone when dissolved in water.

Benzylmethylaniline combines with phenylcarbimide to form *α-phenyl-b-phenyl-b-phenylethylcarbamide*, $\text{NPh}\cdot\text{CO}\cdot\text{NPh}\cdot\text{CHMePh}$, which separates from a mixture of ether and light petroleum in tetragonal, transparent plates and melts at 94—95°.

Diphenylanilinomethane hydrochloride, prepared by adding hydrochloric acid to the product obtained by the action of magnesium phenyl iodide on benzylideneaniline, separates in glistening, green needles and melts at 199°; the free *base*, $\text{NPh}\cdot\text{CHPh}_2$, is a viscid oil.
A. McK.

Electrolytic Preparation of *p*-Aminophenol and its Derivatives. FRIEDRICH DARMSTÄDTER (D.R.-P. 150800).—In the preparation of *p*-aminophenol by the electrolytic reduction of nitrobenzene and other nitro-compounds in which the para-position is unoccupied (Gattermann, Abstr., 1893, i, 566), aniline is also obtained together with the aminophenol when metallic cathodes are employed. This may be avoided by the use of carbon cathodes. A suspension of 100 grams of nitrobenzene in 1 kilogram of 85 per cent. sulphuric acid requires a current density of 4 amperes per sq. decm. C. H. D.

***p*-Aminophenol-*m*-sulphonic Acid.** KALLE & Co. (D.R.-P. 150982).—*p*-Nitroacetylmetanilic acid, $\text{NHAc}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{SO}_3\text{H}$, prepared by nitrating acetylmetanilic acid, forms heavy, sandy crystals. When heated at 100° in closed vessels with solutions of alkali hydroxides or carbonates, it is converted into a mixture of nitroresorcinol and *p*-nitrophenol-*m*-sulphonic acid, which may be separated by acidifying and extracting the nitroresorcinol with ether or benzene, or by neutralising with acid, when the sparingly soluble monosodium salt of nitroresorcinol is precipitated. The acid yields *p*-aminophenol-*m*-sulphonic acid on reduction.
C. H. D.

Action of Zinc Chloride on Acid Esters of Phenols. Acetylcresols. JOHAN F. EIJKMAN (Chem. Centr., 1904, i, 1597; from Chem. Weekblad, 1, 453—461).—4-Acetyl-*m*-cresol (4-acetyl-3-hydroxytoluene), $\text{C}_6\text{H}_3\text{MeAc}\cdot\text{OH}$, prepared by heating a mixture of *m*-cresol and acetyl chloride with zinc chloride for six hours at 140—160°, has an odour similar to that of creosote and forms transparent crystals which melt at 21°; it boils at 103° under 7 mm., at 126° under 20 mm., and at 245° under 760 mm. pressure, has a sp. gr. 1.1012 at 13.1°, n_D 1.5527 at 13.1°, and gives a dark violet coloration with an alcoholic solution of ferric chloride. The *oxime* is readily soluble in benzene

and melts at 103°. The *methyl ether*, $C_{10}H_{12}O_2$, solidifies at 37.2°, boils at 265° under 754 mm. pressure, has a sp. gr. 1.0154 at 78.1°, and n_D 1.50933 at 78.1°. The *oxime* of the methyl ether forms colourless needles, is readily soluble in benzene, and melts at 136°. The *ethyl ether* melts at 71°, boils at 140° under 10 mm. pressure, has a sp. gr. 0.9865 at 78.8° and n_D 1.49989 at 78.8°. The *oxime* of the ethyl ether is readily soluble in benzene and melts at 132°.

6-Acetyl-*m-cresol* (6-acetyl-3-hydroxytoluene), $C_6H_3MeAc\cdot OH$, prepared by allowing a mixture of *m-cresol*, acetyl chloride, and zinc chloride to remain for several weeks at the ordinary temperature, crystallises from alcohol in white, odourless crystals which melt at 128°; it boils at 313° and does not give a coloration with an alcoholic solution of ferric chloride. The *methyl ether* melts at 12°, boils at 150° under 20 mm. and at 268° under 759 mm. pressure, and has a sp. gr. 1.0867 at 15.7° and n_D 1.5503 at 15.7°. The *ethyl ether* melts at 22°, boils at 155° under 18 mm. and at 195° under 81 mm. pressure, and has a sp. gr. 1.0034 at 77.6° and n_D 1.51242 at 77.6°. 6-Acetyl-*m-cresol* and its ethers do not form oximes.

By the action of an alkaline solution of potassium permanganate on the ethers of 4-acetyl-*m-cresol* and 6-acetyl-*m-cresol*, the following derivatives of glyoxylic acid are formed. 2-Methoxy-4-methylphenylglyoxylic acid, $OMe\cdot C_6H_3Me\cdot CO\cdot CO_2H$, prepared from the methyl ether of 4-acetyl-*m-cresol*, melts at 101°. 2-Ethoxy-4-methylphenylglyoxylic acid melts at 144°. 4-Methoxy-2-methylphenylglyoxylic acid, obtained by oxidising the methyl ether of 6-acetyl-*m-cresol*, melts at 85°. 4-Ethoxy-2-methylphenylglyoxylic acid melts at 78°. All the preceding α -ketonic acids crystallise from benzene and, with the exception of 2-ethoxy-4-methylphenylglyoxylic acid, from water or dilute alcohol with $1H_2O$. The corresponding toluic acids are obtained by further oxidation of the acids with manganese dioxide and a 50 per cent. solution of acetic acid, or with glacial acetic acid and a 4 per cent. solution of potassium permanganate.

2-Methoxy-*p-toluic acid*, $OMe\cdot C_6H_3Me\cdot CO_2H$, melts at 104°. 2-Ethoxy-*p-toluic acid* melts at 78.5° (compare Paternò and Canzoneri, *Jahresber.*, 1879, 519). 4-Methoxy-*o-toluic acid* melts at 176°. 4-Ethoxy-*o-toluic acid* melts at 146°.

By the action of excess of hydrogen peroxide on the α -ketonic acids, 2-methoxyterephthalic acid, 2-ethoxyterephthalic acid, 4-methoxyphthalic acid, and 4-ethoxyphthalic acid are formed; the acids melt at 281°, 254°, 167°, and 163° respectively. By the action of zinc chloride and acetyl chloride on resorcinol, acetylresorcinol, $C_6H_3Ac(OH)_2$, and diacetylresorcinol, $C_6H_2Ac_2(OH)_2$, are formed, whilst under similar conditions thymol yields only *p*-acetyl-*o*-thymol, $C_6H_2MePrAc\cdot OH$.

E. W. W.

Cyclic Compounds. GEORGE STADNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 485—489. Compare Markownikoff and Stadnikoff, *Abstr.*, 1903, i, 803).—On heating the heptanaphthylene oxide previously described (*loc. cit.*) with water, it yields methylcyclohexane-3:4-glycol, $CHMe\left<\begin{array}{c} CH_2-CH_2 \\ CH_2\cdot CH(OH) \end{array}\right>CH\cdot OH$, which is a viscous, colourless, odour

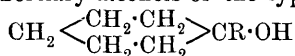
less liquid boiling at 134° under 18 mm. pressure. The *diacetyl* derivative, $C_7H_{12}(OAc)_2$, is a viscous liquid which has a pleasant fruity odour and boils at 157 — 158° under 40 mm. pressure.

Heptanaphthylene dibromide, $C_7H_{12}Br_2$, is a colourless liquid which has a camphor-like odour, boils at 130° under 40 mm. pressure, and has a sp. gr. 1.56 at $15^{\circ}/15^{\circ}$ and 1.648 at $20^{\circ}/15^{\circ}$, and $[\alpha]_D$ $18^{\circ}48'36''$.

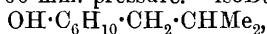
The chloro-ketone prepared by oxidising the chlorohydrin by means of chromic acid boils at 110 — 111° under 40 mm. pressure, and not at 114° as previously stated (*loc. cit.*), and has a sp. gr. 1.106 at $15^{\circ}/15^{\circ}$.

T. H. P.

Synthesis of a New Series of Tertiary Alcohols from cyclo-Hexanol. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1904, 138, 1321—1324).—Tertiary alcohols of the type



are readily obtained from *cyclohexanone* (compare Sabatier and Senderens, this vol., i, 156) by means of the Grignard reaction. These alcohols are insoluble in water, readily soluble in alcohol or ether, and are converted by the action of dehydrating agents into the corresponding olefine, the constitution of which is not at present determined. The following alcohols and olefines were prepared: *methylcyclohexanol* (compare Markownikoff and Tcherdintzeff, *Abstr.*, 1900, i, 578) boils at 68° under 20 mm. pressure and has a sp. gr. 0.953 at $0^{\circ}/0^{\circ}$; the *acetyl* derivative boils at 176° under 760 mm. pressure, and the *phenylurethane*, $C_6H_{10}MeO \cdot CO \cdot NHPh$, crystallises in bright needles and melts at 105° ; by the action of anhydrous zinc chloride at 160° , an *olefine* is obtained boiling at 108° under 760 mm. pressure and having a sp. gr. 0.827 at $0^{\circ}/0^{\circ}$. *Ethylcyclohexanol*, $C_6H_{10}Et \cdot OH$, has an odour of camphor, forms brilliant prisms which melt at 33° , boils at 76° under 20 mm. and at 166° under 760 mm. pressure; the *acetyl* derivative boils at 190° under 760 mm. pressure, and the *phenylurethane* melts at 83° ; the *olefine* obtained by the action of zinc chloride boils at 134° under 760 mm. pressure. *Propylcyclohexanol*, $C_6H_{10}Pr \cdot OH$, is a viscous liquid with an odour like camphor, it boils at 85° under 20 mm. and at 180° under 760 mm. pressure, has a sp. gr. 0.945 at $0^{\circ}/0^{\circ}$, and yields an *olefine* boiling at 154° under 760 mm. pressure. *isoButylcyclohexanol*,



boils at 102° under 20 mm. pressure. *isoAmylcyclohexanol*, $OH \cdot C_6H_{10} \cdot C_5H_{11}$, is a viscous liquid smelling of camphor, boils at 115° under 20 mm. pressure, has a sp. gr. 0.917 at $0^{\circ}/0^{\circ}$, and yields an *olefine* boiling at 194° under 760 mm. pressure and having a sp. gr. 0.856 at $0^{\circ}/0^{\circ}$. *Phenylcyclohexanol*, $C_6H_{10}Ph \cdot OH$, has an agreeable aromatic odour, forms large, thick crystals which melt at 61° , boils at 153° under 20 mm. pressure, and yields an *olefine* boiling at 133° under 20 mm. pressure and having a sp. gr. 1.004 at $0^{\circ}/0^{\circ}$. *p-Tolylcyclohexanol*, $OH \cdot C_6H_{10} \cdot C_7H_7$, is a liquid with an aromatic odour, boils at 151° under 20 mm. pressure, has a sp. gr. 0.995 at $0^{\circ}/0^{\circ}$, forms colourless crystals melting at 0° , and yields an *olefine* boiling at 142° under 20 mm. pressure and having a sp. gr. 0.981 at $0^{\circ}/0^{\circ}$. *Benzyl-*

cyclohexanol, $\text{OH}\cdot\text{C}_6\text{H}_{10}\cdot\text{CH}_2\text{Ph}$, forms colourless crystals melting at 33° , boils at 160° under 20 mm. pressure, and yields an *olefine* boiling at 138° under 20 mm. pressure and having a sp. gr. 0.983 at $0^\circ/0^\circ$. cycloHexylcyclohexanol, $\text{OH}\cdot\text{C}_6\text{H}_{10}\cdot\text{C}_6\text{H}_{11}$, forms white, pearly plates which melt at 51° , boils with decomposition at 148° under 20 mm. pressure, and yields an *olefine* boiling at 124° under 20 mm. pressure and having a sp. gr. 0.923 at $0^\circ/0^\circ$. M. A. W.

Reduction of *o*-Nitrobenzyl Alcohol. General Remarks on the Formation of Indazyl Derivatives. PAUL FREUNDLER (*Compt. rend.*, 1904, 138, 1425—1427).—The author summarises the results already published (compare Abstr., 1903, i, 371, 585; this vol., i, 121, 351). *Indazyl-o-benzyl acetate* forms red needles melting at $39\text{--}40^\circ$ and is decomposed on distillation into phenylindazole and acetic acid.

M. A. W.

Cholesterol. II. ADOLF WINDAUS (*Ber.*, 1904, 37, 2027—2032. Compare this vol., i, 49).—The oxidation of cholestandione, $\text{C}_{27}\text{H}_{42}\text{O}_2$, to cholestanonic acid, $\text{C}_{27}\text{H}_{42}\text{O}_5$, was regarded as analogous to the oxidation of camphor to camphoric acid; confirmation of the view that cholestandione is a cyclic ketone has been obtained by isolating the intermediate products of oxidation, which are analogous to those obtained from suberone.

The intermediate *ketohydroxy-acid*, $\text{C}_{27}\text{H}_{44}\text{O}_4$, prepared by oxidising cholestandione with ammonium persulphate, crystallises from hot acetic acid in prisms, sinters at 185° , and melts at 217° ; the sintering is characteristic of the purified acid and is probably due to gradual conversion into the lactone. The *sodium* salt, $\text{C}_{27}\text{H}_{43}\text{O}_4\text{Na}$, crystallises from 50 per cent. alcohol in large, glistening plates. The *methyl* ester, $\text{C}_{28}\text{H}_{46}\text{O}_4$, separates from petroleum in minute crystals melting at 105° , but does not crystallise at all readily; its *oxime*, $\text{C}_{28}\text{H}_{47}\text{O}_4\text{N}$, however, crystallises readily from methyl alcohol in glistening plates and melts at 148° . The acid is oxidised by chromic acid to cholestanonic acid, showing that the hydroxyl group is in the condition of a primary alcohol.

Dibromocholestandione, $\text{C}_{27}\text{H}_{40}\text{O}_2\text{Br}_2$, crystallises from 80 per cent. alcohol in stout, colourless prisms, and, when rapidly heated, blackens and melts, liberating gas, at about 165° .

Bromocholestanonic acid, $\text{C}_{27}\text{H}_{41}\text{O}_5\text{Br}$, crystallises from 80 per cent. alcohol in lustrous scales, similar to cholesterol, and darkens and melts with liberation of gas at about 151° .

T. M. L.

Action of Magnesium Aryl Haloids on Dicarboxylic Acids. WALTHER DILTHEY and E. LAST (*Ber.*, 1904, 37, 2639—2641. Compare Valeur, Abstr., 1901, i, 317; Gattermann and Maffezzoli, this vol., i, 172).—The action of bromobenzene and magnesium on ethyl oxalate in ethereal solution leads to the formation of β -benzopinacolin, on ethyl succinate in ethereal solution, to the formation of the *glycol*, $\text{OH}\cdot\text{CPh}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CPh}_2\cdot\text{OH}$, which crystallises in needles, melts at 202° , is soluble in alcohol or glacial acetic acid, and dissolves in concentrated sulphuric acid to a red solution.

The *hydroxy-ketone*, $\text{OH}\cdot\text{CPh}_2\cdot\text{CH}_2\cdot\text{COPh}$, is obtained when phenyl magnesium bromide is boiled with ethyl malonate in ethereal solution

and the product treated with acidified ice-water. It crystallises in transparent, colourless nodules, melts and decomposes into acetophenone and benzophenone at 126—127°, decomposes into the same substances when recrystallised from petroleum boiling above 130°, dissolves in concentrated sulphuric acid to a red solution, and forms a yellowish-red solution with hydrogen chloride and stannic chloride in benzene or chloroform solution. G. Y.

Action of Magnesium Methiodide on Piperonal. EFISIO MAMELI (*Gazzetta*, 1904, 34, i, 358—374).—The action of magnesium methiodide on piperonal yields methylpiperonyl ether, methylpiperonyl alcohol, acetopiperone, piperonylethylene, and a polymeride of the last-named compound.

Methylpiperonylcarbinol (β -3:4-methylenedioxyphenylethyl alcohol), $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_3\cdot\text{CHMe}\cdot\text{OH}$, is an oily liquid insoluble in water, but soluble in ether or benzene, and having an odour recalling that of heliotrope; it boils at 139—140° under 22 mm. pressure, partially decomposing into water and piperonylethylene; it has the normal molecular weight in freezing benzene, and on oxidation with permanganate yields acetopiperone; with concentrated sulphuric acid, it gives instantly a solid violet mass, which afterwards becomes purple.

Piperonylethylene (3:4-methylenedioxystyrene),



distils at 108—109° under 20—22 mm. and at 223—225° under the ordinary pressure, being partially transformed in both cases into the polymeride (see *infra*); it does not mix with water, has a peculiar odour and a neutral reaction, and is soluble in benzene or chloroform; it distils in a current of steam and has the normal molecular weight in freezing benzene or acetic acid; it rapidly decolorises bromine and absorbs hydrogen bromide, and with potassium permanganate it yields piperonylic acid; sulphuric acid converts it into a pasty, amorphous mass of a wine-red or violet-red colour; its sp. gr. is 1.158 at 15°; on keeping about a month, it becomes transformed into a gelatinous, viscous mass having the same composition and molecular weight as the original compound. On treatment with hydrogen bromide, it yields *piperonylmonobromoethane* (α -3:4-methylenedioxyphenyl- α -bromoethane), $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_3\cdot\text{CHBrMe}$, which crystallises from benzene or a mixture of benzene and light petroleum in tufts of white prisms melting at 107°. With bromine, it gives *piperonyldibromoethane*, $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_3\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$, crystallising from benzene in spheroidal agglomerates of slender, white needles melting at 160° and dissolving in alcohol.

The polymeride of piperonylethylene, when heated rapidly, begins to fuse and decompose at 210°, bubbles being evolved which increase up to 230° and then diminish, after which a yellow, glassy mass remains.

Dipiperonyldiethyl ether (?), $\text{O}(\text{CHMe}\cdot\text{C}_6\text{H}_3\cdot\text{O}_2\cdot\text{CH}_2)_2$, crystallises from alcohol in tufts of white prisms melting at 111°; it dissolves in benzene or chloroform and to a slight extent in water or ether; it slightly reduces Fehling's solution, but not ammoniacal silver nitrate;

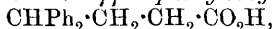
at low concentrations, it gives low values for the molecular weight in benzene, but exhibits normal behaviour in stronger solutions.

T. H. P.

Synthesis of Aromatic Fatty Acids by means of Lactones.

JOHAN F. EIJKMAN (*Chem. Centr.*, 1904, i, 1416; from *Chem. Weekblad*, 1, 421—424).—By the action of γ -valerolactone, $\begin{array}{c} \text{CH}_2\text{---CO} \\ | \quad \diagup \text{O} \\ \text{CH}_2\text{---CHMe} \end{array}$

on benzene in presence of aluminium chloride, γ -phenylvaleric acid, $\text{CHMePh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, is obtained. This acid forms colourless crystals, melts at about 13° , boils at 147° under 2 mm., at 170° under 10 mm., or at 210° under 85 mm. pressure, and has a sp. gr. 1.0554 at 15° . The aluminium salt, $\text{Al}(\text{C}_{11}\text{H}_{13}\text{O}_2)_3$, forms a white, curdy mass. The calcium salt is an amorphous precipitate which is soluble in alcohol or ether, but only sparingly so in water. γ -Tolylvaleric acid, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, prepared in a similar manner by the action of toluene on γ -valerolactone, is a colourless, syrupy liquid which boils at 154° under 2 mm. and at 176° under 10 mm. pressure; it has a sp. gr. 1.0398 at 15° . $\gamma\gamma$ -Diphenylbutyric acid,

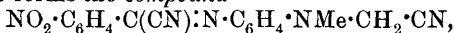


obtained by the action of benzene on γ -phenylbutyrolactone in presence of aluminium chloride, crystallises from alcohol in colourless crystals melting at 107° .

E. W. W.

ω -Cyanodimethylaniline. THEODOR ST. WARUNIS and FRANZ SACHS (*Ber.*, 1904, 37, 2636—2639. Compare *Abstr.*, 1902, i, 780; 1903, i, 335, 336).— ω -Cyanodimethylaniline, $\text{C}_6\text{H}_5\cdot\text{NMe}\cdot\text{CH}_2\cdot\text{CN}$, prepared by heating methylaniline and formaldehydecyanohydrin in a sealed tube at 100° and fractionally distilling the product, forms a colourless liquid, becoming dark, and boiling at 266° . On dissolving in concentrated sulphuric acid, pouring into water, and adding ammonia, phenylmethylglycineamide, $\text{NMePh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, is precipitated, and crystallises from water in white prisms melting at 163° (compare Silberstein, *Abstr.*, 1885, 160); it yields phenylmethylglycine on hydrolysis.

Sodium nitrite and hydrochloric acid convert the nitrile into *p*-nitroso- ω -cyanodimethylaniline, $\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{CH}_2\cdot\text{CN}$, separating from alcohol in green crystals and melting at 114 — 116° . *p*-Nitrobenzyl cyanide forms the compound



separating from dilute alcohol in bright red crystals and melting at 195° .

Nitrous acid converts the glycineamide into methyl-*p*-nitrosophenylglycineamide, $\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, melting at 179° , sparingly soluble in alcohol, insoluble in ether or benzene. Malononitrile forms an azomethine compound melting at 211° ; *p*-nitrobenzyl cyanide forms a brown compound melting at 229° .

Nitrous acid also reacts with anilinoacetonitrile to form a nitrosoamine melting at 51 — 52° . The nitrosoamine of anilinoacetamide, $\text{NO}\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, crystallises from water and melts at 143° .

C. H. D.

Halogen Derivatives of Phenylglycine-*o*-carboxylic Acid. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 148615).—Halogen derivatives of phenylglycine-*o*-carboxylic acid are readily obtained by the action of halogens on phenylglycine-*o*-carboxylic acid suspended in glacial acetic acid.

*Bromophenylglycine-*o*-carboxylic acid* crystallises from alcohol in yellow needles and melts at 228°.

*Chlorophenylglycine-*o*-carboxylic acid* melts at 210—215°. The addition of a further quantity of bromine causes no further substitution in the cold, but the continued passage of chlorine leads to the formation of *dichlorophenyl-*o*-carboxylic acid*, melting at 237—238°.

The same derivatives are obtained by the action of chlorine or bromine on *ω*-cyanomethylantranilic acid and hydrolysis of the products. *Bromo-ω-cyanomethylantranilic acid* forms yellow needles and melts at 209—210°, *chloro-ω-cyanomethylantranilic acid* melts at 199—200°, and *dichloro-ω-cyanomethylantranilic acid* at 222—223°.

C. H. D.

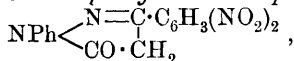
Products of the Hydrolysis of Ethyl 3:5-Dinitrobenzoyl-acetoacetate. LUDWIG BEREND and FRITZ HEYMANN (*J. pr. Chem.*, 1904, [ii], 69, 449—473. Compare Abstr., 1902, i, 470).—3:5-Dinitrobenzoyl chloride boils at 196° under 10—12 mm. pressure.

When treated with 10 per cent. alcoholic ammonia, ethyl 3:5-dinitrobenzoyl-acetoacetate yields 3:5-dinitrobenzamide melting at 183°, ethyl 3:5-dinitrobenzoylacetate, and the ammonium compound of the latter substance.

Ethyl 3:5-dinitrobenzoylacetate crystallises from alcohol in white leaflets and melts at 73°. On evaporation of the alcoholic mother liquor, crystals are obtained which melt at about 173° and on recrystallisation yield the leaflets melting at 73°. The *ammonium* compound is only slightly soluble in water.

When warmed with hydroxylamine hydrochloride and sodium acetate in concentrated aqueous solution, ethyl 3:5-dinitrobenzoyl acetate yields 3-*s*-dinitrophenylisooxazolone,
$$\text{O} \begin{array}{c} \text{N}=\text{C} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2 \\ | \\ \text{CO} \cdot \text{CH}_2 \end{array}$$
, which crystallises in prismatic needles and melts and decomposes at 173—175°.

With phenylhydrazine in glacial acetic acid solution, ethyl 3:5-dinitrobenzoylacetate forms 1-phenyl-3-*s*-dinitrophenyl-5-pyrazolone,



which crystallises in slender, yellow needles and melts at 227°.

When boiled with 30—40 per cent. sulphuric acid, ethyl 3:5-dinitrobenzoyl-acetoacetate yields 3:5-dinitrobenzoylacetone and 3:5-dinitroacetophenone.

3:5-Dinitrobenzoylacetone crystallises in glistening needles and melts at 121°. With hydrazine hydrate in alcoholic solution, it yields 3-*s*-dinitrophenyl-5-methylpyrazole, which crystallises in slender, white needles and melts at 220°.

With phenylhydrazine in glacial acetic acid solution, 3:5-dinitro-

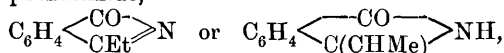
benzoylacetone forms 1-phenyl-3-s-dinitrophenyl-5-methylpyrazole, which crystallises in rhombic plates and melts at 179°.

3:5-Dinitroacetophenone forms an *oxime* which crystallises in white needles and melts at 122°. *m*-Nitrobenzylidene-3:5-dinitroacetophenone, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{CO} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2$, formed by the action of *m*-nitrobenzaldehyde on 3:5-dinitroacetophenone, is a yellow, crystalline powder which melts at 226°.

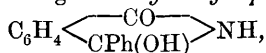
3-Nitro-5-aminoacetophenone, obtained by reduction of dinitroacetophenone with the calculated amount of stannous chloride and hydrochloric acid, crystallises in stellate clusters of needles and melts at 156—158°.

Diacetyldiaminoacetophenone crystallises in white needles, melts at 210°, and is formed by the action of acetic anhydride on 3:5-diaminoacetophenone, which crystallises according to the solvent in clear yellow plates, thick prisms, or stellate groups of needles, and melts at 133—134°. G. Y.

Action of Mixed Organomagnesium Compounds on Phthalimide and Phenylphthalimide. II. CONSTANTIN BÉIS (*Compt. rend.*, 1904, 139, 61—62).—The author discusses the two possible formulæ for the product of the reaction between magnesium ethyl bromide and phthalimide,



obtained by the loss of a molecule of water from the intermediate 3-hydroxy-3-ethylisoindolinone, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{C} \\ \diagdown \quad \diagup \\ \text{CEt(OH)} \end{array} \text{NH}$ (compare this vol., i, 503); in favour of the first formula, it is pointed out that in the case of the substituted phthalimides the hydroxyisoindolinone is always obtained (compare Sachs and Ludwig, this vol., i, 266). The author, however, inclines to the second or isoindolone formula for the following reasons: (1) when the radicle introduced by the organomagnesium compound cannot form an ethylene linking with the carbon atom carrying the hydroxyl group, dehydration does not take place, and the hydroxy-compound is obtained; thus, with phthalimide, magnesium phenyl bromide gives 3-hydroxy-3-phenylisoindolinone,



melting at 160°, soluble in hot water and in the ordinary organic solvents; (2) isobutylisoindolone reacts with magnesium ethyl bromide in the normal manner of compounds containing an NH group; (3) ethylisoindolone and isobutylisoindolone behave like imides in giving silver derivatives of the type $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}(\text{CHMe}) \\ \diagdown \quad \diagup \\ \text{NAg} \end{array}$. M. A. W.

3-Aminophthalanil. HUGO KAUFFMANN and ALFRED BEISSWENGER (*Ber.*, 1904, 37, 2610—2612. Compare Abstr., 1903, i, 700).—

3-Aminophthalanil, $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{C} \\ \diagdown \quad \diagup \\ \text{CO} \end{array} \text{NPh}$, prepared by reducing the nitro-compound with iron and acetic acid, crystallises from acetic acid in long, yellow needles and melts at 180—186°; when crystallised from benzene, it melts at 185—187°. The *acetyl* derivative, $\text{C}_{16}\text{H}_{12}\text{O}_3\text{N}_2$,

crystallises from alcohol in white needles and melts at 191° ; unlike the base, it does not give fluorescent solutions. T. M. L.

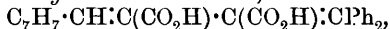
Thermochromic Properties of Dibenzylidenesuccinic Anhydride. (Butadiene Compounds, IV.) HANS STOBBE [and, in part, VICTOR VON VIGIER] (*Ber.*, 1904, 37, 2465—2468).—Dibenzylidenesuccinic anhydride,

$$\begin{array}{c} \text{CHPh}:\text{C}:\text{CO} \\ | \\ \text{CHPh}:\text{C}:\text{CO} \end{array} > \text{O} \quad (\text{this vol., i, 589}),$$
 forms large, triclinic crystals melting at $203\text{--}204^{\circ}$, and lemon-yellow in colour at the ordinary temperature. When cooled to -80° , the colour becomes distinctly lighter, and at -180° in liquid air is a pale sulphur-yellow. The darker yellow colour is gradually restored on warming to the ordinary temperature. On heating, darkening is first observed at 80° , a distinct orange tint is perceptible at 100° , and a brown colour at 160° . The original yellow colour is rapidly restored on cooling. Prolonged heating at 160° produces a further change, and the substance becomes permanently lighter yellow on cooling.

The colour changes are similar to those observed in zinc oxide, potassium chromate, and mercuric cuprous iodide, and occur only in the solid state. Solutions of dibenzylidenesuccinic anhydride in benzene, anisole, and phenetole have the same colour when cold or when boiling. The molecular weight in boiling chloroform and boiling naphthalene is also constant, the compound being in both cases unimolecular. C. H. D.

Triarylbutadienedicarboxylic Acids. (Butadiene Compounds, V.) HANS STOBBE [with PAUL KOHLMANN, PHOKION NAOUM, and KURT KOHLMANN] (*Ber.*, 1904, 37, 2656—2662. Compare Abstr., 1897, i, 192).— $\gamma\gamma$ -Diphenyl- α -benzylideneitaconic acid ($\alpha\delta\delta$ -triphenylbutadiene- $\beta\gamma$ -dicarboxylic acid) is prepared by the condensation of benzaldehyde with ethyl $\gamma\gamma$ -diphenylitaconate by means of sodium ethoxide in alcoholic solution. The acid obtained from the aqueous solution of the sodium salt is white and contains $9\text{H}_2\text{O}$, which is gradually lost at the ordinary temperature, the substance becoming yellow. When crystallised from chloroform, the acid forms white, hexagonal prisms containing chloroform of crystallisation; these crystals rapidly lose chloroform on exposure to air, and become yellow. This yellow acid is found to melt and decompose at $218\text{--}219^{\circ}$, and may be the stable modification of the acid melting at 207° (*loc. cit.*). The sodium, calcium, barium, and piperidine salts are described. The anhydride, $\text{C}_{24}\text{H}_{16}\text{O}_3$, formed by the action of acetyl chloride, crystallises in red prisms and melts, but does not decompose, at 218° . Oxidation of $\gamma\gamma$ -diphenyl- α -benzylideneitaconic acid with potassium permanganate in aqueous potassium carbonate solution leads to the formation of benzophenone and benzoic and oxalic acids.

$\gamma\gamma$ -Diphenyl- α -p-tolylideneitaconic acid,



obtained from p-tolualdehyde and ethyl diphenylitaconate, crystallises in short, yellow prisms or plates, melts at 231° , and dissolves in concentrated sulphuric acid to an orange solution, which becomes green and finally red. The sodium salt contains water of crystallisation; the anhydride, formed by the action of acetyl chloride on the acid, crystallises in red needles and melts at 194° .

δδ-Diphenyl-α-cumylbutadiene-αγ-dicarboxylic acid,
 $C_6H_4Pr^{\beta}\cdot CH:C(CO_2H)\cdot C(CO_2H):CPh_2$,

from cuminaldehyde and ethyl diphenylitaconate, crystallises in short, thick, yellow prisms and melts and decomposes at 229°. The *sodium* salt contains $3H_2O$ and crystallises in white plates; the *anhydride* crystallises in red prisms and melts at 139–140°. G. Y.

Formation of Stereoisomeric Butanedicarboxylic Acids by Reduction of Butadienedicarboxylic Acids. (Butadiene Compounds. VI.) HANS STOBBE and VICTOR VON VIGIER (*Ber.*, 1904, 37, 2662–2670).—Dibenzylidenesuccinic acid is reduced by sodium amalgam in presence of carbon dioxide in aqueous solution to a mixture of *cis*- and *trans*-dibenzylsuccinic acids, the *cis*-acid being the main product. These stereoisomeric acids are separated with difficulty by crystallisation from water or ether. The *trans*-acid is the main product obtained on reduction of *isodibenzylidenesuccinic acid*.

cis-Dibenzylsuccinic acid, $H\cdot\overset{\overset{CO_2H}{|}}{C}-\overset{\overset{CO_2H}{|}}{C}\cdot H$,
 $\quad\quad\quad| \quad\quad\quad|$
 $\quad\quad\quad C_7H_7 \quad C_7H_7$, crystallises in sheaves of needles, melts and decomposes at 203°, and dissolves in concentrated sulphuric acid to a colourless solution which gradually becomes rose-coloured. The *anhydride* formed by the action of acetyl chloride on the acid crystallises in leaflets and melts at 104°.

trans-Dibenzylsuccinic acid, $H\cdot\overset{\overset{CO_2H}{|}}{C}-\overset{\overset{C_7H_7}{|}}{C}\cdot H$,
 $\quad\quad\quad| \quad\quad\quad|$
 $\quad\quad\quad C_7H_7 \quad CO_2H$, crystallises in monoclinic prisms, melts at 204°, decomposes at 207°, and dissolves in concentrated sulphuric acid to a yellowish-green solution. The *anhydride* crystallises in small, six-sided prisms and melts at 155°.

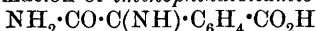
A mixture of the two acids melts at 195° and decomposes at 204°. The *cis*-acid is converted into the *trans*-form when heated with concentrated hydrochloric acid at 180°. Both anhydrides undergo partial isomeric change when heated at 180°.

Reduction of γ -diphenyl- α -benzylideneitaconic acid with sodium amalgam in presence of carbon dioxide in aqueous solution leads to the formation of a mixture of *cis*- and *trans*- $\alpha\delta\delta$ -triphenylbutane- $\beta\gamma$ -dicarboxylic acids, which melts at 175–191° and is resolved into its components when recrystallised from a mixture of ether and low boiling petroleum.

cis- $\alpha\delta\delta$ -Triphenylbutane- $\beta\gamma$ -dicarboxylic acid, $H\cdot\overset{\overset{CO_2H}{|}}{C}-\overset{\overset{CO_2H}{|}}{C}\cdot H$,
 $\quad\quad\quad| \quad\quad\quad|$
 $\quad\quad\quad CH_2Ph \quad CHPh_2$, crystallises in hair-like needles, melts at 175°, and is almost completely converted into the *trans*-modification when heated with concentrated hydrochloric acid at 180°. The *trans*-acid crystallises in prisms and melts at 205°. G. Y.

Methyl Hydrogen Phthalonate. ARTHUR GLOGAU (*Monatsh.*, 1904, 25, 391–396. Compare this vol., i, 249).—Concentrated alcoholic ammonia hydrolyses methyl hydrogen phthalonate (m. p.

79—81°). The action of cold concentrated aqueous ammonia on the ester leads to the formation of *iminophthalonamic acid*,



or $\text{NH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{NH}) \cdot \text{CO}_2\text{H}$, and its *ammonium* salt. The acid crystallises in slender, colourless needles and melts at 191—193°; the ammonium salt melts and decomposes at 218—223° and is insoluble in dilute, aqueous ammonia; the *mercuric* salt is formed as a white precipitate on addition of mercuric chloride in aqueous solution.

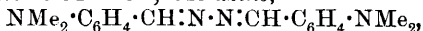
The action of bromine and potassium hydroxide on phthalonic acid and on iminophthalonamic acid leads to the formation of phthalic acid in both cases.

With phenylhydrazine in methyl alcoholic solution, methyl hydrogen phthalonate yields Henrique's methyl phenylphthalazonecarboxylate, which melts at 114° (Abstr., 1888, 824).

The methyl hydrogen phthalonate, which melts at 79—81°, must have the constitution $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CO}_2\text{Me}$. G. Y.

Substituted Benzaldehydes. 2-Chloro-5-nitrobenzaldehyde and *ortho*-Dimethylaminobenzaldehyde. PAUL COHN and ALBERT BLAU (*Monatsh.*, 1904, 25, 365—374).—Reduction of 2-chloro-5-nitrobenzaldehyde (Erdmann, Abstr., 1893, i, 160) with sodium hydrogen sulphite and hydrochloric acid leads to the formation of 2-chloro-5-aminobenzaldehyde hydrochloride, which is amorphous. 2-Chloro-5-acetylaminobenzaldehyde crystallises in glistening, white needles and melts at 163—164°. With dimethylamine in alcoholic solution, 2-chloro-5-nitrobenzaldehyde forms 5-nitro-2-dimethylaminobenzaldehyde, which crystallises in yellow needles and melts at 105°. The *oxime* crystallises in yellow needles and melts at 125°; the *phenylhydrazone* crystallises in dark red needles and melts at 168°; the *hydrochloride* is easily soluble in water; the *platinichloride* is unstable. When boiled with primary aromatic bases in alcoholic solution, 2-chloro-5-nitrobenzaldehyde yields benzylidene derivatives. 2-Chloro-5-nitrobenzylideneaniline crystallises in yellow needles and melts at 103°; 2-chloro-5-nitrobenzylidene-*p*-toluidine crystallises in yellow leaflets and melts at 133°; chloronitrobenzylidene-*o*-toluidine crystallises in glistening scales and melts at 125°; chloronitrobenzylidene-*α*-naphthylamine crystallises in yellow needles, melts at 176°, and is only slightly soluble in alcohol.

o-Dimethylaminobenzaldehyde, formed by the action of methyl sulphate on *o*-aminobenzaldehyde (Abstr., 1903, i, 492), boils at 142° under 30 mm., at 244° under atmospheric pressure. The *platinichloride* crystallises in brown needles; the *oxime* crystallises in white needles and melts at 84—85°; the *azine*,



crystallises in yellow needles, melts at 148—149°, and forms a crystalline *platinichloride*.

Di-o-aminobenzylideneazine, obtained from *o*-aminobenzaldehyde and hydrazine sulphate, crystallises in yellow needles and melts at 248°.

G. Y.

Amino-ketones. ERICH KOLSHORN (*Ber.*, 1904, 37, 2474—2486). — *Phthalimidomethyl ethyl ketone*, $C_6H_4:(CO)_2:N\cdot CH_2\cdot COEt$, prepared by heating chloromethyl ethyl ketone with potassium phthalimide in xylene solution at 135° , crystallises from boiling water in colourless, glistening needles melting at 107° ; on heating it with 20 per cent. hydrochloric acid, the *hydrochloride* of *aminomethyl ethyl ketone* is formed, which crystallises in hygroscopic, rhombic plates melting at about 152° ; the *platinichloride* melts at 169 — 170° . Aminomethyl ethyl ketone acts as a powerful reducing agent towards Fehling's, and with phenylhydrazine forms the ethylglyoxalphenylethylosazone described by Woff (*Abstr.*, 1896, i, 87). It unites with potassium thiocyanate, forming 4-ethylglyoxaline-2-mercaptan, $\begin{array}{c} CEt\cdot NH \\ || \\ CH-N \end{array} \gg C\cdot SH$ or $\begin{array}{c} CEt-N \\ || \\ CH\cdot NH \end{array} \gg C\cdot SH$, which crystallises in colourless plates and on heating softens at 210° , and is not melted by 265° . From this, α or β -ethylglyoxaline is formed on oxidation with nitric acid, of which the following salts are described: the *nitrate*, forming colourless plates, which soften at 78° and melt at $82\cdot5^\circ$; the *aurichloride*, crystallising in thin needles, often in stellar aggregates, melting at 118 — 119° ; and the *picrate* melting at 116° . When condensed with potassium cyanate,

2-hydroxy-4-ethylglyoxaline, $\begin{array}{c} CEt-N \\ || \\ CH-NH \end{array} \gg C\cdot OH$, is formed; this darkens

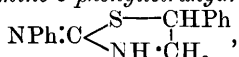
at 157° and melts and decomposes at 166 — 167° . *Benzenesulphamino-methyl ethyl ketone*, $SO_2Ph\cdot NH\cdot CH_2\cdot COEt$, prepared by interaction with benzenesulphonic chloride, forms colourless, rhombic plates, which sinter at 84° and melt at 88 — 89° . On treatment in cold aqueous solution with potassium hydroxide and mercuric chloride, the *mercury* salt of 2:5-diethylpyrazine, $C_8H_{12}N_2\cdot 2HgCl_2$, is formed, decomposing at 168° .

2:5-Diethylpyrazine, $CEt\ll\begin{array}{c} CH\cdot N \\ N\cdot CH \end{array}\gg CEt$, boils at $185\cdot5$ — 186° and solidifies in a freezing mixture; the *aurichloride* sinters at 155° and decomposes at 156 — 157° ; the *picrate* melts at 93° .

The amino-ketone is reduced by sodium amalgam in acid solution to the α -amino- β -butanol recently described by Tordoir (*Abstr.*, 1902, i, 265), boiling at $168\cdot5$ — 170° ; of the derivatives described, the *N-phenylbutylene- ψ -thiocarbamide* [2-phenylimino-5-ethyltetrahydrothiazole], melting at 89 — 90° , is new. With hydrogen bromide, Bookman's (*Abstr.*, 1895, i, 199) β -bromobutylamine is obtained; this sinters at 131° , melts at about 142° , and forms a *picrate* melting at 140° and decomposing at 213° , not at 150° as given by Bookman.

Phenylaminomethylcarbinol is produced among other products on reducing isonitrosoacetophenone with sodium amalgam in acid solution, and has been characterised by the following salts; the *picrate* crystallises in prismatic plates melting at 146 — 147° and decomposing at 205° ; the *platinichloride* darkens at about 200° and is not melted at 260° , whilst the *benzoyl* derivative forms characteristic colourless plates, which sinter at 143° and melt at 144 — $145\cdot5^\circ$. *α -Hydroxy- α -*

phenyl ethyl phenylthiocarbamide, $\text{NPh} \cdot \text{CS} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CHPh} \cdot \text{OH}$, crystallises in needles melting at $131-132^\circ$; *N-phenyl phenethylene- ψ -thiocarbamide* [2-phenylimino-5-phenyltetrahydrothiazole],



crystallises in plates or stars melting at $113-115^\circ$ and forms a picrate melting at $164-165^\circ$.

4-Hydroxy-3-propionylisocarbostyryl, $\text{C}_6\text{H}_4 \begin{array}{l} \text{CO} - \text{NH} \\ \text{C}(\text{OH}) : \text{C} \cdot \text{COEt} \end{array}$, prepared by heating phthalimidomethyl ethyl ketone with sodium in methyl alcohol, crystallises in needles melting at $231-232^\circ$ and forms a *phenylhydrazone*, $(\text{C}_{12}\text{H}_{11}\text{NO}_2) \cdot \text{N}_2\text{HPh}$, melting and decomposing at $212-213^\circ$.
E. F. A.

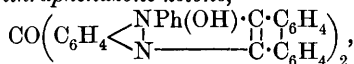
Halogenated Nitro-derivatives of Benzophenone. FORTUNATO CONSONNO (*Gazzetta*, 1904, 34, i, 374-387).—4:4'-Dichloro-3:3'-dinitrobenzophenone, $\text{C}_{13}\text{H}_6\text{O}_4\text{N}_2\text{Cl}_2$, prepared by the action of fuming nitric acid on *p*-dichlorobenzophenone, separates from acetic acid in small crystals melting at 120° and soluble in alcohol, ether, sulphuric acid, or benzene.

4:4'-Dichloro-3:3':5-trinitrobenzophenone, $\text{C}_{13}\text{H}_5\text{O}_6\text{N}_3\text{Cl}_2$, obtained by the action of potassium nitrate on a sulphuric acid solution of *p*-dichlorobenzophenone, is deposited from acetic acid in crystals melting at 140° and dissolves in sodium hydroxide solution yielding a phenol.

3:3'-Dinitro-4:4'-dianilinobenzophenone, $\text{C}_{25}\text{H}_{18}\text{O}_5\text{N}_4$, prepared by the interaction of aniline and 4:4'-dichloro-5:5'-dinitrobenzophenone, separates from acetic acid in orange-yellow crystals melting at 212° and is soluble in alcohol, ether, or benzene, and, with formation of a bright red coloration, in sulphuric acid.

3:3'-Diamino-4:4'-dianilinobenzophenone, $\text{C}_{25}\text{H}_{22}\text{ON}_4$, obtained by reducing the preceding compound in alcoholic solution by means of stannous chloride, is deposited from ether in yellow crystals melting at 160° , and dissolves in alcohol or benzene and in sulphuric acid with formation of a red coloration. Its *hydrochloride* forms green crystals melting at 270° .

Diphenyldiphenanthraphenazone ketone,



obtained by the action of an acetic acid solution of phenanthraquinone on an alcoholic solution of 3:3'-diamino-4:4'-dianilinobenzophenone hydrochloride, separates from dilute alcohol in crystals melting at 220° and dissolves in acetic or sulphuric acid. Its *hydrochloride* forms small, yellowish-red crystals soluble in water.

3:3'-Dinitro-4:4'-diaminobenzophenone, $\text{C}_{13}\text{H}_{10}\text{O}_5\text{N}_4$, prepared by the action of alcoholic ammonia on 4:4'-dichloro-5:5'-dinitrobenzophenone, forms golden-yellow crystals melting at 121° and dissolves in alcohol, ether, benzene, hydrochloric or sulphuric acid.

3:3':4:4'-Tetra aminobenzophenone, $\text{C}_{13}\text{H}_{14}\text{ON}_3$, obtained by reducing

the preceding compound by means of stannous chloride and hydrochloric acid, crystallises from alcohol in yellow needles melting at 155° and is soluble in ether, benzene, acetic or sulphuric acid.

Diphenanthraphenazine ketone, $\text{CO}\left(\text{C}_6\text{H}_4\left\langle\begin{smallmatrix} \text{N}\cdot\text{C}\cdot\text{C}_6\text{H}_4 \\ \text{N}\cdot\text{C}\cdot\text{C}_6\text{H}_4 \end{smallmatrix}\right\rangle\right)_2$, prepared by the action of an acetic acid solution of phenanthraquinone on the preceding compound, separates from alcohol in brownish-yellow crystals decomposing at 160° and is soluble in acetic acid, and, with formation of a bright red solution, in sulphuric acid.

4 : 4'-*Dichloro-3 : 3' : 5 : 5'-tetranitrobenzophenone*, $\text{C}_{13}\text{H}_4\text{O}_9\text{N}_4\text{Cl}_2$, obtained by the action of potassium nitrate on a fuming sulphuric acid solution of 4 : 4'-dichloro-3 : 3'-dinitrobenzophenone, is deposited from acetic acid in crystals melting at 202° .

3 : 3' : 5 : 5'-*Tetranitro-4 : 4'-dianilinobenzophenone*, $\text{C}_{25}\text{H}_{16}\text{O}_9\text{N}_6$, prepared by the action of aniline on the preceding compound, separates from acetic acid in golden-yellow crystals melting at 262° and is soluble in alcohol, ether, benzene, or sulphuric acid.

3 : 3' : 5 : 5'-*Tetranitro-4 : 4'-dihydroxybenzophenone*, $\text{C}_{13}\text{H}_6\text{O}_{11}\text{N}_4$, obtained by the interaction of 4 : 4'-dichloro-3 : 3' : 5 : 5'-tetranitrobenzophenone, alcohol, and aqueous sodium carbonate, is deposited from alcohol in yellow crystals melting at 203° and is soluble in water, ether, acetic or sulphuric acid.

3 : 3' : 5 : 5'-*Tetranitro-4 : 4'-diaminobenzophenone*, $\text{C}_{13}\text{H}_8\text{O}_9\text{N}_6$, prepared by the action of alcoholic ammonia on 3 : 3' : 5 : 5'-tetranitro-4 : 4'-dichlorobenzophenone, forms yellow crystals melting at 270° and is soluble in alcohol, benzene, acetic or sulphuric acid.

3 : 3' : 5 : 5'-*Tetranitrotetramethyl-4 : 4'-diaminobenzophenone*, $\text{C}_{17}\text{H}_{16}\text{O}_9\text{N}_6$, obtained by the action of dimethylamine on an alcoholic solution of tetranitrobenzophenone (melting at 202°), forms yellow crystals melting at 234° .

3 : 3'-*Dinitro-4 : 4'-dimethoxybenzophenone*, $\text{C}_{15}\text{H}_{12}\text{O}_7\text{N}_2$, prepared by the action of sodium methoxide on 4 : 4'-dichloro-5 : 5'-dinitrobenzophenone, separates in yellow crystals melting at 205° and is slightly soluble in alcohol or benzene and more so in sulphuric acid.

3 : 3'-*Dinitro-4 : 4'-diethoxybenzophenone*, $\text{C}_{17}\text{H}_{16}\text{O}_7\text{N}_2$, separates from acetic acid or alcohol in crystals melting at 132° .

3 : 3'-*Dinitro-4 : 4'-dihydroxybenzophenone*, $\text{C}_{13}\text{H}_8\text{O}_7\text{N}_2$, prepared by the action of potassium hydroxide on either of the two preceding compounds or by the action of aqueous sodium carbonate and alcohol on 4 : 4'-dichloro-3 : 3'-dinitrobenzophenone, is deposited from alcohol in yellow crystals melting at 172° and dissolves in benzene, in alkalis giving a red, and in sulphuric acid a bright red coloration.

3 : 3'-*Dinitro-4 : 4'-dimethylaminobenzophenone*, $\text{C}_{15}\text{H}_{14}\text{O}_5\text{N}_4$, obtained by the action of an alcoholic solution of methylamine on 4 : 4'-dichloro-3 : 3'-dinitrobenzophenone, separates from alcohol or acetic acid in yellow crystals melting at 212° .

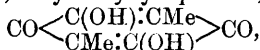
3 : 3'-*Dinitrotetramethyl-4 : 4'-diaminobenzophenone*, $\text{C}_{17}\text{H}_{18}\text{O}_5\text{N}_4$, is deposited from acetic acid in yellow crystals melting at 150° and dissolves in alcohol, benzene, or sulphuric acid giving a red solution.

T. H. P.

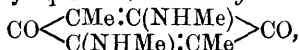
Homologues of ψ -Ionone Hydrate. PIERRE COULIN (D.R.-P. 150771. Compare Abstr., 1903, i, 837).—The method employed for the preparation of ψ -ionone hydrate may also be applied to its homologues. Thus, methyl- ψ -ionone, prepared by condensing citral with methyl ethyl ketone, yields, with phosphoric acid at a low temperature, *methyl- ψ -ionone hydrate*, having a sp. gr. 0.950 at 20°, boiling at 186—192° under 12.5 mm. pressure and forming an oily *semicarbazone*. The mixture of ketones obtained by condensing citral with methyl ethyl ketone in presence of dilute sodium hydroxide forms a *hydrate* having a sp. gr. 0.956 at 20°, boiling at 185—195° under 13.5 mm. pressure, and forming a crystalline *semicarbazone* which melts at 193°. Ethyl- ψ -ionone, prepared from citral and methyl propyl ketone, forms a *hydrate* having a sp. gr. 0.950 and boiling at 198—205° under 17.5 mm. pressure. C. H. D.

Synthesis of Dialkylated Dihydroxyquinones. FRITZ FICHTER and ADOLF WILLMANN (Ber., 1904, 37, 2384—2390).—3 : 6-Dihydroxy-2 : 5-diethylquinone, $\text{CO} \begin{smallmatrix} \text{Cet}:\text{C}(\text{OH}) \\ \text{C}(\text{OH}):\text{Cet} \end{smallmatrix} \text{CO}$, obtained as a by-product in the preparation of ethyl ethylloxalacetate by the action of sodium on an ethereal solution of ethyl oxalate and ethyl butyrate, crystallises from alcohol or acetic acid in minute flakes, from benzene in needles, has a yellowish-red colour, gives a bluish-violet solution in sulphuric acid, is very volatile, sublimes at 196° under 15 mm. pressure, and melts at 217—218° when heated in a sealed tube. It dissolves in alkali hydroxides to a violet solution, but is reprecipitated on acidifying. The *diacetate*, $\text{C}_{14}\text{H}_{16}\text{O}_6$, crystallises from alcohol in yellow needles and melts at 130°. The *dibenzoate*, $\text{C}_{24}\text{H}_{20}\text{O}_6$, crystallises from benzene in minute spangles and melts at 201°. Reduction and acetylation gives *tetra-acetoxy-p-diethylbenzene*, $\text{C}_6\text{Et}_2(\text{OAc})_4$, which crystallises from alcohol in colourless, glistening flakes and melts at 213°. Reduction of the diacetate just described gives *tetrahydroxy-p-diethylbenzene diacetate*, $\text{C}_6\text{Et}_2(\text{OH})_2(\text{OAc})_2$, which crystallises from alcohol in colourless needles and melts at 205°. When fused with benzoic anhydride, this gives the *tetrabenzoate*, $\text{C}_6\text{Et}_2(\text{OBz})_2$, which separates from acetic acid in colourless crystals and melts at 275°.

The lower homologue, dihydroxyxyloquinone,



was prepared by Arnold (Diss. Würzburg, 1888) by a method similar to that described above, and its constitution has been established also by preparing it from xyloquinone. *Dimethyldiaminoxyloquinone*,



the intermediate substance prepared by the action of methylamine on xyloquinone, crystallises from benzene or alcohol, melts at 227°, and yields the dihydroxy-compound when hydrolysed by 33 per cent. sulphuric acid.

3 : 6-Dihydroxy-2 : 5-diisopropylquinone, $\text{CO} \begin{smallmatrix} \text{CPr}^i:\text{C}(\text{OH}) \\ \text{C}(\text{OH}):\text{CPr}^i \end{smallmatrix} \text{CO}$,

crystallises from acetic acid in dark red plates, melts in a sealed tube at 154° , sublimes at 165 — 168° under 15 mm. pressure, and gives a bluish-violet solution in concentrated sulphuric acid. The *diacetate*, $C_{18}H_{26}O_6$, crystallises from alcohol in yellow needles and melts at 137.5° . *Tetra-acetoxydiisopropylbenzene*, $C_6Pr_2^B(OAc)_4$, prepared by reducing and acetylating the diacetate, crystallises from alcohol in colourless, glistening flakes and melts at 245° . T. M. L.

Yellow Dyes of the Anthracene Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 151384).—Bromoanilinoanthraquinonesulphonic acid, prepared by adding bromine to anilinoanthraquinonesulphonic acid made into a paste with water, condenses with aromatic amines on heating in a closed vessel, forming green dyes. Further sulphonation furnishes dark green sulphonic acids. The halogen derivatives prepared in glacial acetic acid solution do not yield similar condensation products. C. H. D.

New Anthracene Dyes. PAUL FRIEDLÄNDER and GEORG SCHICK (*Zeit. Farb. Text. Ind.*, 1904, 3, 218—221. Compare this vol., i, 69).—When dihydroquinizarin is heated with an excess of *p*-toluidine in presence of boric acid (D.R.-P. 91152), a 1:4-*di-p*-toluidinodihydroanthraquinone, $C_6H_4 \begin{smallmatrix} C(OH) \\ > \\ C(OH) \end{smallmatrix} C_6H_2(NH \cdot C_7H_7)_2$, is formed, which rapidly oxidises to 1:4-*di-p*-toluidinoanthraquinone (*quinizarin-green*), which crystallises from glacial acetic acid in long, slender, indigo-blue needles and melts at 218° . When dihydroquinizarin is heated with 4—5 times its weight of *p*-toluidine in presence of very little hydrochloric acid, quinizarin-blue (1-*hydroxy-4-p*-toluidinoanthraquinone), $C_6H_4 \cdot (CO)_2 \cdot C_6H_2(OH) \cdot NH \cdot C_7H_7$, is formed.

Anthraquinone-green GX is probably 1:4-*di-p*-toluidinoanthraquinonedisulphonic acid,

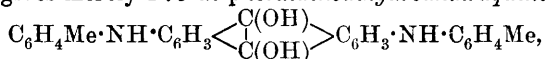
$SO_3H \cdot C_6H_3 \cdot (CO)_2 \cdot C_6H_2(NH \cdot C_7H_7) \cdot NH \cdot C_7H_6 \cdot SO_3H$
 $[NH \cdot C_7H_7 : NH \cdot C_7H_6 \cdot SO_3H : SO_3H = 1 : 4 : 7]$; on reduction with stannous chloride and hydrochloric acid, it gives *p*-toluidine, *p*-toluidinesulphonic acid, and *dihydroquinizarin-6(1)-sulphonic acid*, which is isolated in the form of its barium salt. Anthraquinone-green GX may be obtained by methods which confirm this view. 1-Nitroanthraquinone-6-sulphonic acid is converted by *p*-toluidinesulphonic acid at 200° into 1-sulpho-*p*-toluidinoanthraquinone-6-sulphonic acid,

$SO_3H \cdot C_6H_3 \cdot (CO)_2 \cdot C_6H_3 \cdot NH \cdot C_7H_6 \cdot SO_3H$;
 this, on bromination, gives a 4-bromo-derivative, the bromine atom of which is replaceable by the *p*-toluidino-radicle to form anthraquinone-green GX (D.R.-P. 137566, 138166, 138542).

Alizarin-pure-blue is 2-bromo-1-amino-4-sulpho-*p*-toluidinoanthraquinone, $C_6H_4 \cdot (CO)_2 \cdot C_6HBr(NH_2) \cdot NH \cdot C_6H_3Me \cdot SO_3H$; on reduction with stannous chloride, it gives hydroquinizarin and *p*-toluidinesulphonic acid, the bromine atom being eliminated. The dye can be obtained by converting α -aminoanthraquinone by the direct action of bromine vapour into its 2:4-dibromo-derivative, which melts at 221° , and condensing the product with *p*-toluidine; a 2-bromo-1-amino-4-*p*-toluidinoanthraquinone is obtained, which crystallises from glacial acetic acid

or benzene in long needles, melts at 212° , and on sulphonation gives alizarin-pure-blue.

It appears that it is only the 1:4-diaminoanthraquinone dyes that are converted, on reduction by stannous chloride, into the corresponding 1:4-dihydroxy-derivatives; 1:5-di-*p*-toluidinoanthraquinone on reduction gives merely 1:5-di-*p*-toluidinodihydroanthraquinone,



which crystallises from xylene in brownish-yellow needles and melts at 207° . W. A. D.

Action of Formaldehyde on Menthol. EDGAR WEDEKIND and KARL GREIMER (*Zeit. angew. Chem.*, 1904, 17, 705—711).—The only mentholformaldehyde compounds which are definitely characterised are dimethyl methylene ether, melting at 57° , and menthyl chloromethyl ether, boiling at 160 — 162° under 16 mm. pressure, although various other substances are described in the literature as belonging to this class.

The product described as a mentholformaldehyde compound of the type $\text{C}_{10}\text{H}_{19}\cdot\text{O}\cdot\text{CH}_2\cdot\text{OH}$, and obtained by boiling menthol with an aqueous solution of formaldehyde and dilute hydrochloric acid (D.R.-P. 7278, iv/120), is shown to be a mixture of 2—3 per cent. of menthyl chloride, 3—6 per cent. of menthyl chloromethyl ether, 31—44 per cent. of menthol, and 51—60 per cent. of dimethyl methylene ether. It is improbable in any case that a menthyl hydroxymethyl ether, $\text{C}_{10}\text{H}_{19}\cdot\text{O}\cdot\text{CH}_2\cdot\text{OH}$, is stable, since it would most likely be decomposed by the action of water to form menthol and formaldehyde. Attempts to produce it from menthyl chloromethyl ether and silver oxide were accordingly unsuccessful. A. McK.

Preparation of Solid Camphene. CHEMISCHE FABRIK AUF AKTIEN FORM. E. SCHERING (D.R.-P. 149791).—Solid camphene, free from chlorine, is obtained on heating pinene hydrochloride, hydrobromide, or hydriodide with alcoholic ammonia at 220° . Gaseous or aqueous ammonia may also be employed. When alcohol is used, a small quantity of isobornyl ethyl ether is simultaneously formed. C. H. D.

Chemistry of Caoutchouc and its Distillation Products. RUDOLF DITMAR (*Ber.*, 1904, 37, 2430—2434).—The crude oil resulting from the dry distillation of caoutchouc was submitted to fractional distillation. The behaviour of the various fractions boiling at 35 — 70° , 70 — 150° , 150 — 200° , 200 — 300° , and more than 300° respectively, towards concentrated nitric acid was different. The first four fractions yielded resins, whilst the fifth yielded a monobasic dinitro-acid, which was also isolated in small amount from both the third and fourth fractions. The nitric acid reaction for caoutchouc is also characteristic for sesqui-, di- and poly-terpenes. A. McK.

Acid Number of Colophony. KARL DIETERICH (*Arch. Pharm.*, 1904, 242, 255).—Polemical. A reply to Tschirch (*ibid.*, 106, footnote). C. F. B.

Preparation of Benzoylarbutin. CARL VILMAR (D.R.-P. 151036).—When arbutin is benzoylated according to the general method for glucosides, employing an excess of benzoyl chloride, penta-benzoylarbutin is obtained. The monobenzoyl derivative, however, may be prepared by adding benzoyl chloride slowly to an aqueous solution of arbutin, the latter always being in excess, and neutralising from time to time. *Benzoylarbutin* is precipitated, and after crystallisation from hot water forms slender needles and melts at 184.5° . It dissolves in 1800 parts of water at 9° , in 1300 parts at 15° , and in 80 parts at 100° , is almost tasteless, and is readily hydrolysed by alkalis or magnesia. C. H. D.

Rhamnosides. ERNST SCHMIDT (*Arch. Pharm.*, 1904, 242, 210—224).—This rhamnoglucoside is possibly identical with globularia-citrin from *Globularia alypum* (R. Tiemann, Abstr., 1903, ii, 608).

[With H. BRAUNS.]—Sophorin and caper-rutin from the flower-buds of *Sophora japonica* and *Capparis spinosa* respectively (compare Wachs, Abstr., 1894, i, 299) are shown to be identical with rutin (from *Ruta graveolens*).

[With N. WALIASCHKO.]—Robinin, from the flowers of *Robinia pseudacacia* (Perkin, Trans., 1902, 81, 473), loses 15.4 per cent. of its weight when dried in a desiccator or in the steam-oven, and then has the composition $C_{33}H_{40}O_{19} \cdot \frac{1}{2}H_2O$; its hydrolysis to robigenin, rhamnose, and galactose is expressed by the equation: $C_{33}H_{40}O_{19} + 3H_2O = C_{15}H_{10}O_6 + 2C_6H_{12}O_5 + C_6H_{12}O_6$. Robigenin, $C_{15}H_{10}O_6 \cdot H_2O$, is yellow and melts at $268-270^{\circ}$; it forms a colourless *tetra-acetyl* derivative melting at $182-183^{\circ}$; possibly it is identical with the rhamnolutin from the berries of *Rhamnus cathartica* (Tschirch and Polacco, Abstr., 1900, i, 681). In the mother liquor from the crude robinin, lævorotatory asparagine was found in considerable quantity. C. F. B.

Blue Sulphur Dyes. LEOPOLD CASSELLA & Co. (D.R.-P. 150553).—Brilliant blue dyes are obtained by fusing 4-phenylamino-4'-hydroxydiphenylamine or 4-phenylaminophenyl-4'-hydroxytolylamine with sodium sulphide and sulphur. The products form dark blue powders, insoluble in water, but dissolving in solutions of alkali sulphides, and differ from the corresponding dyes from alkylated aminohydroxydiphenylamines in their greater fastness towards light. C. H. D.

Optical Isomerides of β -Dihydrofuran-2:5-dicarboxylic Acids. HENRY B. HILL and F. W. RUSSE (*Ber.*, 1904, 37, 2538—2540. Compare Hill and Wheeler, Abstr., 1901, i, 556).— β -Dihydrofuran-2:5-dicarboxylic acid can be resolved into its optical antipodes by separating the *l*-acid in the form of its sparingly soluble cinchonine salt and the *d*-acid in the form of its strychnine salt. The *d*-acid has $[\alpha]_D + 480.7^{\circ}$ with $c = 10.15$; $+ 485.4^{\circ}$ with $c = 5.08$; $+ 489.2^{\circ}$ with $c = 2.525$; $+ 502^{\circ}$ with $c = 0.629$; $+ 519^{\circ}$ with $c = 0.157$. The *l*-acid has $[\alpha]_D - 478.7^{\circ}$ with $c = 10.04$; $- 483.4^{\circ}$ with $c = 5.01$; $- 488.3^{\circ}$ with

$c = 2.517$; -507° with $c = 0.627$; -533° with $c = 0.158$. Both acids crystallise with $1\text{H}_2\text{O}$ and melt when anhydrous at 144° ; the barium salts crystallise with $1\frac{1}{2}\text{H}_2\text{O}$, the lead salts with $2\text{H}_2\text{O}$. W. A. D.

9-Diphenylxanthen. FRITZ ULLMANN and GADIEN ENGEL (*Ber.*, 1904, 37, 2367—2374).—Methyl *o*-phenoxybenzoate boils at 312° and not at 360° (Arbenz, *Abstr.*, 1890, 892). *o*-Phenoxytriphenyl carbinol, $\text{OPh}\cdot\text{C}_6\text{H}_4\cdot\text{CPh}_2\cdot\text{OH}$, prepared from it by Grignard's method, crystallises from light petroleum in long, white, silky needles and melts at 120° .

9-Diphenylxanthen, $\text{O} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CPh}_2$, prepared by the action of a mixture of sulphuric and acetic acids on the preceding compound, crystallises from hot acetic acid, melts at 200° , has no basic properties, and does not dissolve in strong acids.

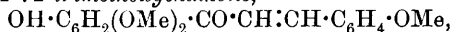
9-Phenylxanthidrol, $\text{O} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CPh}\cdot\text{OH}$, prepared from xanthone by Grignard's method, crystallises from benzene in large, glistening, transparent prisms, melts at 158° , and dissolves in strong acids giving yellow, fluorescent solutions which probably contain the oxonium salts. *9-Phenylxanthen*, $\text{O} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CHPh}$, prepared by reducing with zinc and acetic acid, crystallises from alcohol in large, pointed, pearly crystals and melts at 145° .

4'-Amino-9-diphenylxanthen, $\text{O} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CPh}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, was prepared by heating phenylxanthidrol with aniline hydrochloride and acetic acid; the hydrochloride forms long, silky, asbestos-like needles, darkens at 260° , and melts and decomposes at $262\text{--}263^\circ$; the base separates from alcohol in large, glistening, colourless crystals and melts at 227.5° ; the diazo-compound is converted by the action of cuprous oxide into diphenylxanthen. *4'-Dimethylamino-9-diphenylxanthen*, $\text{O} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CPh}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, crystallises from acetic acid in glistening, colourless crystals and melts at 195.5° . T. M. L.

A Second Synthesis of Luteolin. S. FAINBERG and STANISLAUS VON KOSTANECKI (*Ber.*, 1904, 37, 2625—2627. Compare *Abstr.*, 1899, i, 370, and this vol., i, 517).—5 : 7 : 3' : 4'-Tetramethoxyflavanone reacts with bromine in chloroform solution to form 3 : 6 : 8-tribromo-5 : 7 : 3' : 4'-tetramethoxyflavanone, $\text{C}_6\text{Br}_2(\text{OMe})_2 \begin{smallmatrix} \text{O} \\ \text{CO} \end{smallmatrix} \begin{smallmatrix} \text{CH} \\ \text{CH} \end{smallmatrix} \text{C}_6\text{H}_3(\text{OMe})_2$, which crystallises from a mixture of benzene and alcohol in white needles and melts and decomposes at 200° . On addition of hot alcohol and potassium hydroxide to its solution in benzene, white needles of 6 : 8-dibromo-5 : 7 : 3' : 4'-tetramethoxyflavone, $\text{C}_6\text{Br}_2(\text{OMe})_2 \begin{smallmatrix} \text{O} \\ \text{CO} \end{smallmatrix} \begin{smallmatrix} \text{CH} \\ \text{CH} \end{smallmatrix} \text{C}_6\text{H}_3(\text{OMe})_2$, melting at $261\text{--}262^\circ$, are precipitated. The finely-powdered compound is boiled for 4—5 hours with concentrated hydriodic acid, poured into a solution of sodium hydrogen sulphite, and the product

acetylated. The tetra-acetyl-luteolin thus obtained is hydrolysed by boiling with hydriodic acid, poured into sodium hydrogen sulphite, and recrystallised from dilute alcohol. The luteolin (5:7:3':4'-tetrahydroxyflavone) thus obtained is identical with that prepared synthetically by Kostanecki, Rozycki, and Tambor (Abstr., 1901, i, 92). C. H. D.

7:8:2'-Trihydroxyflavonol. S. S. COHEN and STANISLAUS VON KOSTANECKI (*Ber.*, 1904, 37, 2627—2631).—Salicylaldehyde methyl ether and gallacetophenone dimethyl ether condense together in warm alcoholic solution in presence of sodium hydroxide, forming 2'-hydroxy-3':4':2-trimethoxychalkone,



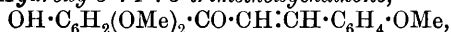
crystallising from alcohol in bright yellow needles melting at 105°, and dissolving in concentrated sulphuric acid to an orange-red solution. The *acetyl* derivative forms white needles and melts at 88°.

When the condensation is carried out at the boiling temperature, the chalkone obtained is mixed with the sparingly soluble 7:8:2'-trimethoxyflavanone, $\text{C}_6\text{H}_2(\text{OMe})_2\left\langle\begin{array}{c} \text{O}-\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe} \\ \text{CO}\cdot\text{CH}_2 \end{array}\right.$, which crystallises from alcohol in large, colourless prisms, melts at 112°, and dissolves in concentrated sulphuric acid or alcoholic potassium hydroxide to orange-red solutions. The chalkone may also be converted into the flavanone derivative by heating with dilute hydrochloric acid.

isoNitroso-7:8:2'-trimethoxyflavanone, $\text{C}_{18}\text{H}_{17}\text{O}_6\text{N}$, from the flavanone, amyl nitrite, and hydrochloric acid, crystallises from alcohol in thick, yellow tablets and melts and decomposes at 170°. When dissolved in acetic acid and boiled with dilute sulphuric acid, it forms 7:8:2'-trimethoxyflavonol, crystallising from alcohol in white needles and melting at 212—214°. It forms a yellow sodium salt, and dissolves in sulphuric acid to a greenish-yellow solution. It produces only a faint yellow shade with aluminium mordants. The *acetyl* derivative forms white needles and melts at 138—139°.

Concentrated hydriodic acid converts the trimethoxyflavonol into 7:8:2'-trihydroxyflavonol, $\text{C}_6\text{H}_2(\text{OH})_2\left\langle\begin{array}{c} \text{O}-\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{OH} \\ \text{CO}\cdot\text{C}\cdot\text{OH} \end{array}\right.$, which crystallises from very dilute alcohol in pale yellow needles, melts and decomposes at 298°, and dissolves in dilute sodium hydroxide to a reddish-yellow solution. In accordance with its constitution, it yields brilliant orange shades with aluminium mordants and brown or black shades with iron mordants (compare Katschalowsky and Kostanecki, this vol., i, 608). C. H. D.

7:8:3'-Trihydroxyflavonol. STANISLAUS VON KOSTANECKI and O. SCHLEIFENBAUM (*Ber.*, 1904, 37, 2631—2633. Compare preceding abstract).—2'-Hydroxy-3':4':3-trimethoxychalkone,



prepared by the condensation of *m*-methoxybenzaldehyde with gallacetophenone dimethyl ether, crystallises from alcohol in yellow

needles and melts at 127—128°. The *acetyl* derivative forms pale yellow needles and melts at 80—81°.

7 : 8 : 3'-*Trimethoxyflavanone*, $C_{18}H_{18}O_6$, forms white needles and melts at 79°. Its *isonitroso*-derivative crystallises from alcohol in broad, pale yellow needles and melts and decomposes at 168°. It yields a brownish-yellow shade with cobalt mordants.

7 : 8 : 3'-*Trimethoxyflavonol*, $C_{18}H_{16}O_6$, forms pale yellow needles and melts at 188—189°. It forms a yellow sodium salt and produces a pale yellow shade with aluminium mordants. The *acetyl* derivative forms slender, white needles and melts at 165°.

7 : 8 : 3'-*Trihydroxyflavonol*, $C_6H_2(OH)_2 \begin{smallmatrix} \text{O} \\ | \\ \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OH} \\ | \\ \text{CH} \cdot \text{C} \cdot \text{OH} \end{smallmatrix}$, forms pale yellow needles containing water and melts at 260°. It dyes strong orange shades with aluminium mordants, and brown or black shades with iron mordants. The *tetra-acetyl* derivative forms white needles and melts at 166—167°. C. H. D.

Synthesis of Flavanone. STANISLAUS VON KOSTANECKI and W. SZABRAŃSKI (*Ber.*, 1904, **37**, 2634—2635).—Flavanone has not hitherto been prepared, the method employed for its attempted synthesis having yielded the isomeric 2'-hydroxychalkone. The latter may, however, be converted into flavanone by the general method devised by Kostanecki and Lampe (this vol., i, 441) of boiling the alcoholic solution with dilute mineral acid.

Flavanone, $C_6H_4 \begin{smallmatrix} \text{O} - \text{CHPh} \\ | \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix}$, crystallises from dilute alcohol in small, colourless needles having a faint aromatic odour, and melts at 75—76°. Concentrated sulphuric acid dissolves it to a slightly yellow solution, and alcoholic sodium hydroxide to an orange solution.

Bromine in carbon disulphide solution forms *α-bromoflavanone*, which was not isolated in a pure state. Potassium hydroxide converts this into flavone, thus confirming the constitution of flavanone, and also providing a new synthesis of flavone (compare Feuerstein and Kostanecki, *Abstr.*, 1898, i, 583; Kostanecki and Tambor, *Abstr.*, 1900, i, 239). C. H. D.

The Thiophen Reaction with Nitrous-sulphuric Acid. CARL LIEBERMANN and BERNHARD PLEUS (*Ber.*, 1904, **37**, 2461—2464).—The failure to obtain the Liebermann thiophen reaction with samples of coke-oven benzene (Schwalbe, this vol., i, 337) is shown to be due to the small quantity of thiophen in such benzene. The reaction with nitrous-sulphuric acid fails when the proportion of thiophen falls below 0.1 per cent., whereas the isatin reaction is obtained with only 0.01 per cent. A quantitative determination by Dimroth's method (*Abstr.*, 1899, i, 428) showed the Ludwigshafen benzene to contain only 0.077 per cent. of thiophen.

Contrary to Bauer's statement (this vol., i, 519), the indophenine reaction is obtained with pure sulphuric acid free from nitrogen (compare Storch, this vol., i, 610).

[With F. MAUTHNER.]—Indophenine forms *indopheninesulphonic acid*,

$C_{12}H_6NOS \cdot SO_3H$, when heated with sulphuric acid, dissolving in pure water to a blue solution and precipitated by acids. It forms a sparingly soluble *barium* salt, $(C_{12}H_6O_4NS_2)_2Ba$. C. H. D.

Some Liquid Alkaloids. FRIEDRICH W. SEMMLER (*Ber.*, 1904, 37, 2428—2430).—Determinations of the molecular refraction of the base, $C_{10}H_{17}ON$, previously described (this vol., i, 437, 602) led to the conclusion that the substance in question is a saturated keto-imine having no double linking, and not an unsaturated keto-amine with a double linking. The molecular refraction of coniine, nicotine, and sparteine respectively has now been determined in order to test whether this physical method has any practical use as an aid to determining the constitution of the various liquid alkaloids under consideration.

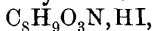
Coniine has the sp. gr. 0.8440 at 20° , n_D 1.4505, and M_D 40.51, values in accordance with Brühl's, which agreed with the representation of coniine as a cyclic saturated imine.

Nicotine has the sp. gr. 1.011 at 20° , n_D 1.5270 at 20° , and M_D 49.2, values also in agreement with those of Brühl and in agreement with the theoretical figures.

Sparteine has the sp. gr. 1.0199 at 20° , n_D 1.5291, and M_D 70.8, whilst the latter value, calculated for the formula $C_{15}H_{26}N_2$ on the assumption that there is no double linking, and that the nitrogen atoms are tertiary, should be 70.8. It is concluded that the sparteine molecule contains four rings (compare Willstätter and Marx, this vol., i, 613).

A. McK.

Damascenine. HERBERT POMMERHNE (*Arch. Pharm.*, 1904, 242, 295—298. Compare *Abstr.*, 1899, i, 964; 1900, i, 684; 1901, i, 289).—Of the substance that remains when methyl is eliminated from damascenine by the agency of hydriodic acid, the *hydriodide*,



melting at 198 — 200° , and the *hydrochloride*, with $\frac{1}{2}H_2O$, melting at 217 — 218° when dried, were analysed.

Damascenine is transformed by boiling with baryta water into the same acid substance that is formed when alcoholic potash is used; the *barium* salt obtained has the composition $(C_9H_{10}O_3N)_2Ba$, $C_9H_{11}O_3N$.

When oxidised with barium permanganate at the ordinary temperature, damascenine yields oxalic acid, ammonia, and methylamine.

C. F. B.

Alkine Esters. CHININFABRIK BRAUNSCHWEIG; BUCHLER & Co. (D.R.-P. 151189).—Alkines combine with the haloids of organic alkyloxy- or acetoxy-acids. When acid chlorides are employed, they are best prepared by means of thionyl chloride. The products closely resemble the difficultly prepared, unsubstituted alkine esters in their physiological action.

Acetyltropyltropine, from acetyltropyl chloride and tropine hydrochloride, forms a syrup crystallising slowly and readily hydrolysing to atropine. *Acetyltropyl-lupineine*, from acetyltropyl chloride and lupinine hydrochloride, has similar properties. *Bromohydratropyltropine*, from bromohydratropyl bromide and tropine hydrobromide, is crystalline

and melts at 180°. *m*-Acetoxybenzoyltropeine forms a colourless oil, yielding a crystalline *platinichloride*. *Opianyl-lupineine* melts at 100°. C. H. D.

Preparation of Xanthine Derivatives. C. F. BOEHRINGER & SÖHNE (D.R.-P. 151133).—The 8-methyl group may be removed from 8-trichloromethylxanthines (this vol., i, 340) by boiling with water,

$$\begin{array}{c} \text{NR} \cdot \text{CO} \cdot \text{C} \cdot \text{NR} \\ | \qquad | \\ \text{CO} \cdot \text{NR} \cdot \text{C} - \text{N} \end{array} \begin{array}{c} \text{H} \\ | \\ \text{C} \end{array} \begin{array}{c} \text{H} \\ | \\ \text{C} \end{array} \text{CCl}_3 + 2\text{H}_2\text{O} = \text{CO}_2 + 3\text{HCl} + \begin{array}{c} \text{NR} \cdot \text{CO} \cdot \text{C} \cdot \text{NR} \\ | \qquad | \\ \text{CO} \cdot \text{NR} \cdot \text{C} - \text{N} \end{array} \begin{array}{c} \text{H} \\ | \\ \text{C} \end{array} \text{CH}.$$

Since 8-methylxanthines may be prepared from uric acid and its homologues (Abstr., 1902, i, 125), this reaction affords a means of synthesising the xanthine group. Thus theobromine is obtained from 8-trichloromethyltheobromine, and theophylline from 8-trichloromethyl-7-chloromethyl-1:3-dimethylxanthine by boiling with water, formaldehyde being eliminated in the latter case. Caffeine is obtained from 8-trichloromethylcaffeine by boiling with water or acetic acid or by fusing with dry oxalic acid. C. H. D.

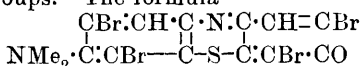
Syntheses of Derivatives of Quinoline. EDWARD BARTOW and ELMER V. MCCOLLUM (*J. Amer. Chem. Soc.*, 1904, 26, 700—705).—6-Methylquinoline and 8-nitro-6-methylquinoline can be prepared by Knueppel's modification of Skraup's synthesis, in which arsenic oxide is used as the oxidising agent.

The following compounds were prepared by the action of acetaldehyde on an aromatic amine in presence of hydrochloric acid. 8-Nitro-2:6-dimethylquinoline, obtained from *m*-nitro-*p*-toluidine, crystallises from alcohol in orange-coloured needles and melts at 114°; its *hydrochloride* is described. 6-Chloro-2-methylquinoline, prepared from *p*-chloroaniline, crystallises in white flakes, which turn yellow on exposure to the air, and melts at 91°; its *hydrochloride* was obtained as a white powder. 5-(or 7-)Chloro-2-methylquinoline, obtained from *m*-chloroaniline, is a crystalline substance which melts at 78°. 8-Chloro-2-methylquinoline, prepared from *o*-chloroaniline, forms white crystals and melts at 64°; this compound may also be obtained by the action of glycol on *o*-chloroaniline in presence of arsenic oxide. 6-Bromo-2-methylquinoline, prepared from *p*-bromoaniline, is readily volatile with steam and crystallises from the distillate, melts at 96—97°, and darkens on exposure to the air. E. G.

Polyhydroxyanthraquinonequinolines. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 149781).—1-Aminoanthraquinone-5- or -8-sulphonic acid may be heated with lime under pressure, forming the corresponding aminohydroxyanthraquinones, which may be converted into quinoline derivatives by heating with glycerol, sulphuric acid, and nitrobenzene or picric acid. The 1:5-derivative is a greyish-yellow powder, dissolving in organic solvents to yellow solutions and forming a red sodium salt. Fuming sulphuric acid converts it into a *sulphonic acid*, which yields a *polyhydroxyanthraquinonequinoline* on heating with lime under pressure. This is a sparingly

soluble, dark brown powder, forming blue or violet salts with alkalis. The 1 : 8-derivatives have similar properties. C. H. D.

Immedial-Pure-Blue. ROBERT GNEHM and FELIX KAUFLEDER (*Ber.*, 1904, 37, 2617—2623).—The substance prepared by melting *p*-dimethylamino-*p*-hydroxydiphenylamine with sulphur and sodium sulphide was oxidised with potassium bromate and hydrogen bromide to a compound, $C_{14}H_8ON_2SBr_4$, which was crystallised from nitrobenzene, gave a normal molecular weight in this solvent, and appears to contain two methyl groups. The formula



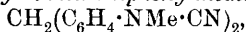
is suggested, and this is in accord with the behaviour of the product towards acetic anhydride and towards reducing agents, but it could not be prepared by the action of bromine on methylene-violet.

When the blue was heated in a sealed tube for 4 hours at 130° with sodium chlorate and hydrochloric acid, it was oxidised to tetrachloroquinone, of which a 20 per cent. yield was obtained. T. M. L.

Reactions in the Triphenylmethane Series. EDUARD VONGERICHTEN and K. WEILINGER (*Zeit. Farb. Text. Ind.*, 1904, 3, 217—218. Compare Vongerichten and Bock, *Abstr.*, 1903, i, 721).—*p*-Diaminotriphenylmethane, when heated with *o*-toluidine and *o*-toluidine hydrochloride for 5 hours at 170° , is converted into *p*-diaminophenyldi-*o*-tolylmethane, which melts at 121 — 122° and gives a *diacetyl* derivative crystallising from alcohol in nodular aggregates and melting at 265 — 266° ; the *tetra-acetyl* derivative, $C_{28}H_{30}O_4N_2$, crystallises from alcohol, melts at 165 — 166° , and is hydrolysed by alcoholic sodium methoxide to the *diacetyl* derivative.

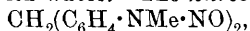
On heating *p*-diaminophenyldi-*o*-tolylmethane with an excess of aniline and aniline hydrochloride, it is reconverted into *p*-diaminotriphenylmethane, which melts at 136 — 137° ; its *diacetyl* derivative crystallises from benzene with $1C_6H_6$ and melts at 234 — 235° ; the *tetra-acetyl* derivative, $C_{27}H_{26}O_4N_2$, melts at 172 — 173° . W. A. D.

Basic Diphenylmethane and Triphenylmethane Dyes. II. Some Derivatives of *para*-Diaminodiphenylmethane. JULIUS VON BRAUN and E. KAYSER (*Ber.*, 1904, 37, 2670—2678; see this vol., i, 344).—*Dicyanodimethyldiaminodiphenylmethane*,

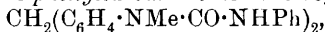


is formed when cyanogen bromide is slowly added to partially fused tetramethyldiaminodiphenylmethane. It separates from glacial acetic acid as a white, glistening, crystalline powder, melts at 155° , is readily soluble in hot alcohol, but is insoluble in ether or acids. It is oxidised by chromic acid in glacial acetic acid solution to *dicyanodimethyldiaminobenzophenone*, $CO(C_6H_4 \cdot NMe \cdot CN)_2$, which is a white, crystalline substance, melts at 236° , and is soluble only in glacial acetic acid. The *oxime*, $OH \cdot N:C(C_6H_4 \cdot NMe \cdot CN)_2$, melts at 173° . The ketone does not react with tertiary bases in presence of phosphorus oxychloride, nor with magnesium phenyl bromide.

s-Dimethyldiaminodiphenylmethane is formed when the dicyano-compound is boiled for some hours with dilute hydrochloric or sulphuric acids, or is dissolved in boiling concentrated hydrochloric acid and gradually diluted with water. The *nitroso*-compound,



melts at 97—98°; the *phenylcarbamide* derivative,



melts at 186—187°; the *phenylthiocarbamide* derivative melts at 153°. The action of methyl iodide on dimethyldiaminodiphenylmethane leads to the formation of tetramethyldiaminodiphenylmethane. With benzyl chloride, the *s*-dimethyl base yields *dibenzyl*dimethyldiaminodiphenylmethane, $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{CH}_2\text{Ph})_2$, which melts at 50°, dissolves in organic solvents or in dilute acids to slightly blue solutions, and forms a *picrate* which melts at 93°.

s-Dimethyldiaminobenzophenone, $\text{CO}(\text{C}_6\text{H}_4\cdot\text{NHMe})_2$, is obtained by hydrolysing dicyanodimethyldiaminobenzophenone with boiling hydrochloric acid. It melts at 130°, and dissolves readily in alcohol, benzene, chloroform, or dilute acids to yellow solutions. The *platinichloride* crystallises in prisms. The action of cyanogen bromide leads to the re-formation of the colourless dicyano-compound. The *nitroso*-compound, $\text{CO}(\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{NO})_2$, melts at 228—229°; the *benzoyl* derivative forms small, white crystals and melts at 204°. G. Y.

Formation of Trialkylated Amidines. JULIUS VON BRAUN (*Ber.*, 1904, 37, 2678—2685).—The action of phosphorus pentachloride on dialkylated amides in chloroform solution leads to the formation of phosphorus oxychloride and the amide chloride, which is precipitated as a crystalline mass on addition of ether or petroleum of low boiling point, or when the chloroform solution is strongly cooled. These amide chlorides may be boiled in chloroform solution or recrystallised from petroleum of low boiling point without decomposition. With water, the amide chlorides react energetically, re-forming the dialkylated amide; with primary amines, trialkylated amidines are formed. The following compounds have been prepared by this method. Dimethylbenzamide chloride, which melts at 36°; phenyldimethylbenzamidine, from dimethylbenzamide; phenylbenzylmethylbenzamidine, from phenylmethylbenzamide, which boils at 331—332°. *Methyl anthranilate dimethylbenzamidine*, $\text{NMe}_2\cdot\text{CPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$, from dimethylbenzamide, phosphorus pentachloride, and methyl anthranilate, forms glistening crystals and melts at 109°; the *picrate*, $\text{C}_{17}\text{H}_{18}\text{O}_9\text{N}_2\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, melts at 111—112°; the *platinichloride* is obtained as an orange precipitate. *Phenyldiethylbenzamidine*, from diethylbenzamide, is an oil which boils at 188—189° under 10 mm. pressure; the *picrate* melts at 114°; the *platinichloride* crystallises in glistening, red needles and melts at 206°. Contrary to Claus' statement (*Ber.*, 1882, 15, 1285), diphenylbenzamide reacts with phosphorus pentachloride in chloroform solution and forms *diphenylbenzamide chloride*, which reacts with aniline to form triphenylbenzamidine; this is a yellow, crystalline powder, melts at 170°, and has slight basic properties. Diphenylbenzamide chloride and *o*-anisidine form

diphenyl-o-anisylbenzamidine, $\text{NPh}_2 \cdot \text{CPh} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, which forms a *picrate* melting at $202-203^\circ$.

Piperidylphenylbenzamidine, $\text{NPh} \cdot \text{CPh} \cdot \text{C}_5\text{NH}_{10}$, formed by the action of phosphorus pentachloride and aniline on benzoylpiperidine, or by the action of piperidine on benzanilideimide chloride, is an oil. The *picrate* melts at $174-175^\circ$; the *platinichloride* crystallises in red needles and melts at 203° .

p-Phenetyldimethyl- α -naphthamidine, $\text{NMe}_2 \cdot \text{C}(\text{C}_{10}\text{H}_7) \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt}$, prepared by acting with phosphorus pentachloride and phenetidine on dimethyl- α -naphthoamide, crystallises in white masses, melts at 150° , and is only slightly soluble in organic solvents. The *platinichloride* forms red, matted needles and melts at 220° .

Dimethyl- α -naphthoamide, formed by the action of α -naphthoic chloride on dimethylamine, melts at 62° and boils at $207-208^\circ$ under 15 mm. pressure. G. Y.

Phenylhydrazino-oxalic Hydrazide and its Derivatives. CARL BÜLOW (*Ber.*, 1904, 37, 2424—2428).—The monophenylhydrazide of ethyl oxalate, $\text{NHPh} \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{Et}$ (1 mol.), and hydrazine hydrate (1 mol.) yield, in alcoholic solution, *phenylhydrazino-oxalic hydrazide*, $\text{NHPh} \cdot \text{NH} \cdot \text{CO} \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$, which separates in glistening needles and melts at $205-206^\circ$. It is soluble in cold dilute hydrochloric acid and more so in dilute aqueous potassium hydroxide. It shows marked amphoteric characteristics and may possibly have the constitution $\text{NHPh} \cdot \text{N} \cdot \text{C}(\text{OH}) \cdot \text{C}(\text{OH}) \cdot \text{N} \cdot \text{NH}_2$; it reduces both Fehling's solution and silver nitrate. Its *acetyl* derivative melts at $220-221^\circ$ and is insoluble in dilute hydrochloric acid, but soluble in potassium hydroxide. Phenylhydrazino-oxalic hydrazide condenses with benzaldehyde to form the *hydrazone*, $\text{NHPh} \cdot \text{NH} \cdot \text{CO} \cdot \text{CO} \cdot \text{NH} \cdot \text{N} \cdot \text{CHPh}$, which crystallises in glassy needles and melts at $249-250^\circ$.

Ethyl 1-phenylhydrazido-oxalamino-2:5-dimethylpyrrole-3:4-dicarboxylate, $\text{NHPh} \cdot \text{CO} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_4\text{NMe}_2(\text{CO}_2\text{Et})_2$, prepared by heating a mixture of phenylhydrazino-oxalic hydrazide and ethyl diacetylsuccinate (compare Bülow, *Abstr.*, 1903, i, 196) in glacial acetic acid, separates in needles and melts at $194-195^\circ$. It is easily soluble in concentrated hydrochloric acid and in dilute potassium hydroxide solution. Its solution in concentrated sulphuric acid turns magenta-red when ferric chloride is added. A. McK.

Action of Phenylbenzylhydrazine on Sugars. RUDOLF OFNER (*Ber.*, 1904, 37, 2623—2625).—The osazone obtained by Neuberg (*Abstr.*, 1902, i, 264) by the action of phenylbenzylhydrazine on lævulose, and also, contrary to Neuberg's statement, from phenylbenzylhydrazine and dextrose, is shown to be a mixed phenyl phenylbenzyl-osazone, $\text{C}_{28}\text{H}_{28}\text{O}_4\text{N}_4$. Its production is due to the fact that commercial phenylbenzylhydrazine always contains phenylhydrazine. Pure phenylbenzylhydrazine does not react with dextrose or lævulose, but Neuberg's osazone is precipitated on the addition of phenylhydrazine to the solution. The same osazone is obtained by the action of phenylbenzylhydrazine on phenyldextrosazone. Votoček's statement (*Zeit. Zuckerind. Böhm.*, 1903, 27, 708) that secondary aromatic hydr-

azines do not react with aldoses, but react with their phenylhydrazones, is therefore correct. C. H. D.

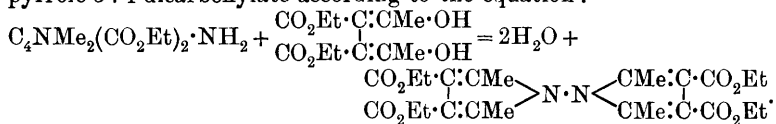
Melting Point of Glycuronic Acid Semicarbazone. G. GIEMSA (*Zeit. physiol. Chem.*, 1904, 41, 548. Compare Abstr., 1901, i, 11; and Fromm, this vol., ii, 360).—The author adheres to his previous statement that the semicarbazone of glycuronic acid lactone, when carefully heated, melts and decomposes at 188—189°.

J. J. S.

Ethyl *N*-Amino-2:5-dimethylpyrrole-3:4-dicarboxylate as the Parent Substance for the Preparation of *N*-Bispyrrole Derivatives. CARL BÜLOW and CONSTANTIN SAUTERMEISTER (*Ber.*, 1904, 37, 2697—2702).—By the action of hydrazine on ethyl $\alpha\beta$ -diacetylpropionate, Korschun (this vol., i, 614) has obtained ethyl 3:6-dimethyl-4:5-dihydropyridazine-4-monocarboxylate, previously described by Bülow (Abstr., 1903, i, 196), and a second product, which gave, on hydrolysis, an acid which is possibly *N*-bis-2:5-dimethylpyrrole-3-(or 4)-carboxylic acid.

The authors have studied the formation of *N*-bisethyl-2:5-dimethylpyrrole-3:4-dicarboxylate, $\text{CO}_2\text{Et}\cdot\text{C}:\text{CMe} > \text{N}:\text{N} < \text{CMe}:\text{C}\cdot\text{CO}_2\text{Et}$ from Bülow's ethyl 1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate.

Ethyl diacetylsuccinate reacts with ethyl 1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate according to the equation:



N-Bisethyl 2:5-dimethylpyrrole-3:4-dicarboxylate, thus obtained, separates from alcohol in colourless needles or stellate leaflets and melts at 126—127°. It may also be prepared from ethyl diacetylsuccinate (2 mols.) and hydrazine hydrate (1 mol.).

N-Bis-2:5-dimethylpyrrole-3:4-dicarboxylic acid, prepared by hydrolysing the preceding ester, crystallises with $1\text{H}_2\text{O}$ and becomes anhydrous at 80—92°; when quickly heated, the anhydrous acid does not melt or decompose below 290°; when heated for 6—7 hours at 100—120°, it suffers very slight decomposition, carbon dioxide being evolved. It does not give a sharp end-point when titrated with phenolphthalein. A. McK.

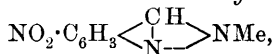
Formation of Indazoles from Nitrated *o*-Methylated Amines. EMILIO NOELTING (*Ber.*, 1904, 37, 2556—2597).—3-Nitrotolueneazo-7-

nitroindazole, $\text{NO}_2\cdot\text{C}_6\text{H}_3 < \begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{NH} > \text{N}:\text{N}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NO}_2$, prepared by

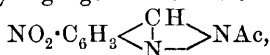
diazotising nitrotoluidine [$\text{CH}_3:\text{NH}_2:\text{NO}_2 = 1:2:3$], crystallises from acetic acid in orange-coloured needles and melts at 250—251°.

The 7-nitroindazole, $\text{NO}_2\cdot\text{C}_6\text{H}_3 < \begin{array}{c} \text{CH} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{NH}$, from which it is derived, melts at 186.5—187.5°, is volatile with steam, and readily

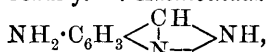
sublimes in yellow needles. 7-Nitro-2-methylindazole,



prepared by the action of methyl sulphate on the indazole, crystallises from alcohol in yellow needles, melts at 144—145°, and is very stable towards hydrolysing agents. 7-Nitro-2-acetylindazole,

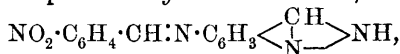


crystallises from a mixture of benzene and light petroleum in white flakes melting at 131—132°, but, after repeated crystallisation from dilute alcohol, the melting point is raised to 186·5—187·5°; the compound decomposes very readily. 7-Aminoindazole,



prepared by reducing the nitro-compound with ferrous hydroxide or ammonium sulphide, crystallises from dilute alcohol in silvery-white flakes, melts at 155—156°, and becomes red when exposed to the light.

The *diacetyl* derivative, $\text{NHAc} \cdot \text{C}_6\text{H}_3 \left\langle \begin{array}{c} \text{CH} \\ | \\ \text{N} \end{array} \right\rangle \text{NAc}$, crystallises from alcohol in needles or prisms, from benzene in plates, and melts at 160·5—161·5°. The *p*-nitrobenzylidene derivative,



separates from alcohol in golden-yellow needles and melts at 227—229°.

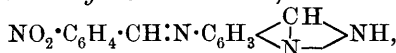
The *hydrochloride* of 6-nitroindazole (Witt, Noetting, and Grandmougin, Abstr., 1891, 312) melts at 168·5—169·5°, becomes solid again at 173° (liberation of hydrogen chloride and separation of the indazole), and again melts at 178—179° (m. p. of indazole, 181°); it is decomposed by water and by alcohol, and was prepared by the action of hydrogen chloride on a solution of the indazole in benzene. The *platinichloride*, $(\text{C}_7\text{H}_5\text{O}_3\text{N}_3)_2, \text{H}_2\text{PtCl}_6$, forms yellow needles, is decomposed by water, and was therefore prepared from a solution of the indazole in a mixture of acetic anhydride and acetic acid. The *platinichloride* of the methylated indazole, $(\text{C}_8\text{H}_7\text{O}_3\text{N}_2)_2, \text{H}_2\text{PtCl}_6$, is decomposed by water and by alcohol, but was prepared from a 20 per cent. solution of hydrogen chloride, from which it separated in yellow crystals. 2-Benzyl-6-nitroindazole, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \left\langle \begin{array}{c} \text{CH} \\ | \\ \text{N} \end{array} \right\rangle \text{N} \cdot \text{CH}_2\text{Ph}$, crys-

tallises from methyl alcohol in long, yellow needles and melts at 111—112°. 2-Benzoyl-6-nitroindazole, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \left\langle \begin{array}{c} \text{CH} \\ | \\ \text{N} \end{array} \right\rangle \text{NBz}$, crystallises from alcohol in white, felted needles, melts at 165—165·5°, and is more stable than the acetyl derivative, although readily hydrolysed by dilute sodium hydroxide. The polymeric *nitrotolueneazo-*

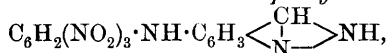
nitroindazole, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \left\langle \begin{array}{c} \text{C} \\ | \\ \text{N} \end{array} \right\rangle \text{N}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NO}_2$, a by-product in

the preparation of the indazole, forms brownish-yellow spangles and

decomposes at a high temperature without melting. The diazoamino-compound, $\text{NO}_2 \cdot \text{C}_7\text{H}_5 \cdot \text{N} : \text{N} \cdot \text{NH} \cdot \text{C}_7\text{H}_5 \cdot \text{NO}_2$, is also formed under certain conditions. The *platinichloride*, $\text{C}_7\text{H}_7\text{N}_3 \cdot \text{H}_2\text{PtCl}_6$, of 6-aminoindazole, $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH} \begin{smallmatrix} \text{CH} \\ | \\ \text{N} \end{smallmatrix} \text{NH}$ (W. N. & G., *loc. cit.*), crystallises in yellow needles. The *p*-nitrobenzylidene derivative,



crystallises from alcohol and melts at $215-216^\circ$. The *dimethyl-p*-aminobenzylidene derivative, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} \cdot \text{C}_6\text{H}_3 \cdot \text{CH} \begin{smallmatrix} \text{CH} \\ | \\ \text{N} \end{smallmatrix} \text{NH}$, crystallises from benzene in yellow crystals with a blue lustre and melts at $198-199^\circ$; it dyes silk and cotton (the latter with tannin mordant) an intense yellow; it is hydrolysed again by long boiling in acid solution. A double compound of 6-aminoindazole and *trinitrobenzene*, $\text{C}_7\text{H}_7\text{N}_3 \cdot \text{C}_6\text{H}_3(\text{NO}_2)_3$, separates from absolute alcohol in long, ruby-red needles and melts at $153-154^\circ$. *Dinitrophenyl-6-indazolyamine*, $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_3 \cdot \text{CH} \begin{smallmatrix} \text{CH} \\ | \\ \text{N} \end{smallmatrix} \text{NH}$, prepared by the action of chlorodinitrobenzene on the base, crystallises from a mixture of alcohol and benzene in reddish-yellow needles and melts at 161° ; it is a weak yellow dye for silk and wool. The *trinitrophenyl* derivative,



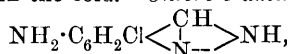
prepared by the action of picryl chloride on the amine, crystallises from a mixture of alcohol and benzene in orange-coloured needles, begins to decompose at 240° , and becomes liquid between 240° and 250° .

4-Nitroindazole, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH} \begin{smallmatrix} \text{CH} \\ | \\ \text{N} \end{smallmatrix} \text{NH}$, crystallises from boiling water in colourless, silky needles, dissolves in alkalis, is only slightly volatile in steam, and melts at 203° . Hydrogen chloride precipitates the *hydrochloride* from benzene in colourless flocks. The *platini-chloride*, prepared in the same way as that of 6-nitroindazole, forms yellow needles and resembles its isomeride. *4-Nitro-2-methylindazole*, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH} \begin{smallmatrix} \text{CH} \\ | \\ \text{N} \end{smallmatrix} \text{NMe}$, prepared by the action of methyl sulphate on the indazole, crystallises from alkaline water in yellow needles, melts at $81-82^\circ$, is readily soluble in alcohol, can be distilled, dissolves in 15 per cent. hydrochloric acid, and is stable towards alkali hydroxides even when heated. The *benzoyl* derivative, $\text{C}_{14}\text{H}_9\text{O}_3\text{N}_3$, crystallises in colourless needles and melts at $162-163^\circ$.

5-Nitroindazole, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH} \begin{smallmatrix} \text{CH} \\ | \\ \text{N} \end{smallmatrix} \text{NH}$, crystallises in colourless, silky needles, melts at 208° , is sparingly volatile with steam, and dissolves in alkalis. *5-Nitro-2-methylindazole*, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH} \begin{smallmatrix} \text{CH} \\ | \\ \text{N} \end{smallmatrix} \text{NMe}$, crystallises from a mixture of benzene and light petroleum in yellow needles, melts at $128-129^\circ$, and is soluble in hydrochloric acid of

12 per cent. strength and above. The *platinichloride* forms yellow needles and is decomposed by water and alcohol, but can be crystallised from dilute hydrochloric acid.

5-Nitro-2-acetylindazole, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \left\langle \begin{smallmatrix} \text{CH} \\ | \\ \text{N} \end{smallmatrix} \right\rangle \text{NAc}$, crystallises from acetic anhydride in snow-white needles and melts at $158-159^\circ$; the acetyl group is removed by boiling in aqueous alcoholic solution or by potassium hydroxide in the cold. *Chloro-5-aminoindazole*,



prepared by reducing the nitroindazole with stannous chloride and hydrogen chloride (chlorination accompanies reduction), crystallises from boiling water in silky spangles and melts at $172-173^\circ$.

7-Nitro-4-methylindazole, $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Me} \left\langle \begin{smallmatrix} \text{CH} \\ | \\ \text{N} \end{smallmatrix} \right\rangle \text{NH}$, crystallises from alcohol in golden, glistening needles and melts at $180-181^\circ$.

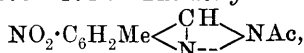
6-Nitro-4-methylindazole forms yellowish-white needles and melts at $177-178^\circ$.

5-Nitro-4-methylindazole forms yellowish-white needles, is only sparingly soluble in acetic acid, and melts at 259° .

6-(or 4)-Nitro-7-methylindazole; a mixture of the isomerides is obtained, and can be separated by fractional crystallisation from water; the less soluble isomeride melts at 222.5° , the more soluble at $175-176^\circ$; the respective constitutions are not determined.

4:6-Dinitro-7-methylindazole, $\text{C}_6\text{HMe}(\text{NO}_2)_2 \left\langle \begin{smallmatrix} \text{CH} \\ | \\ \text{N} \end{smallmatrix} \right\rangle \text{NH}$, crystallises from alcohol in long, pale yellow prisms and melts and decomposes at 200° ; hydrogen chloride precipitates the hydrochloride from benzene.

6-Nitro-5-methylindazole crystallises from water in pale yellow needles and melts at $173-174^\circ$. The *acetyl* derivative,



forms colourless needles and melts at $182-183^\circ$.

4-Nitro-5-methylindazole closely resembles its isomerides and melts at $198-199^\circ$.

4:6-Dinitro-5-methylindazole, $\text{C}_6\text{HMe}(\text{NO}_2)_2 \left\langle \begin{smallmatrix} \text{CH} \\ | \\ \text{N} \end{smallmatrix} \right\rangle \text{NH}$, crystallises from methyl alcohol in colourless needles and melts at $190-191^\circ$.

7-Nitro-6-methylindazole separates from alcohol, water, or benzene in minute, yellow needles or flakes, and from methyl alcohol in long, well-formed prisms, melts as low as 162° , is somewhat volatile with steam, and sublimes in long, slender, amber-yellow prisms. *7-Amino-6-methylindazole* crystallises in snow-white, felted needles and melts and blackens at 194° .

4-Nitro-6-methylindazole crystallises from dilute acetic acid in colourless needles and melts at $206-207^\circ$.

5-Nitro-6-methylindazole melts at $231-232^\circ$. The *acetyl* derivative forms colourless needles, melts at $203-204^\circ$, and is easily hydrolysed.

p-Nitroxyleneol acetate, $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Me}_2 \cdot \text{OAc}$, obtained as a by-product, crystallises from alcohol in pale yellow prisms and melts at $72-73^\circ$.

5 : 7-Dinitro-6-methylindazole crystallises in colourless needles and melts at 229° .

4- or 6-Nitro-5 : 7-dimethylindazole melts at $180-181^\circ$.

4 : 6-Dinitro-5 : 7-dimethylindazole crystallises from alcohol in yellowish-white needles and melts at 247° .

7-Nitro-5 : 6-dimethylindazole crystallises from benzene in pale yellow needles and melts at $180.5-181.5^\circ$.

4-Nitro-5 : 6-dimethylindazole crystallises from benzene in white, silvery flakes and melts at 204° .

4 : 7-Dinitro-5 : 6-dimethylindazole crystallises from anisole in silky, greenish-white needles ; the crude product melted at 208° , but no melting point is given for the recrystallised substance. A table is given showing the properties of all the nitrated indazoles, with the bases from which they are derived, and the yields of indazole with four different methods of decomposing the diazo-compound. T. M. L.

Pyrazolones Derived from α -Mono-substituted Acetoacetic Esters. RENÉ LOCQUIN (*Bull. Soc. chim.*, 1904, [iii], 31, 760—762. Compare Rothenburg, *Abstr.*, 1895, i, 686, and Bouveault and Locquin, this vol., i, 551).—The following pyrazolones were obtained by the condensation of the appropriate ester with hydrazine hydrate. 3-Methyl-4-propyl-5-pyrazolone, $\text{C}_7\text{H}_{12}\text{ON}_2$, crystallises in slender needles from a mixture of alcohol and light petroleum or from boiling dilute alcohol and melts and sublimes at $212-213^\circ$ (corr.). 3-Methyl-4-isobutyl-5-pyrazolone forms slender needles, melts at 237° (corr.), is soluble in boiling alcohol or boiling water, slightly so in ether, and insoluble in light petroleum. 3-Methyl-4-n-amyl-5-pyrazolone crystallises in brilliant lamellæ from dilute alcohol or boiling benzene and melts at $186-187^\circ$ (corr.): the isomeride prepared from ethyl isoamylacetoacetate crystallises in spangles and melts at $217-218^\circ$ (corr.). 3-Methyl-4-n-octyl-5-pyrazolone separates from boiling benzene in lamellæ with a metallic lustre, melts at 182° (corr.), and is readily soluble in light petroleum. 3-Methyl-4-sec-octyl-5-pyrazolone crystallises by spontaneous evaporation of its solution in ether, melts at 137° (corr.), and is slightly soluble in light petroleum. T. A. H.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. VIII. Conversion of the *s*-Dibromobenzoylhydrazines into Derivatives of Furódiazole [Oxadiazole], and Thiodiazole. ROBERT STOLLÉ and AKOP JOHANNISSIEN (*J. pr. Chem.*, 1904, [ii], 69, 474—481. Compare *Abstr.*, 1903, i, 721 ; this vol., i, 102, 200, 453).—To prepare the *s*-dibromobenzoylhydrazines, the acid is treated with phosphorus pentachloride, the product shaken with ice-water to remove hydrogen chloride and phosphorus oxychloride, and the ethereal solution of the acid chloride so obtained shaken with hydrazine sulphate and excess of sodium hydroxide solution.

s-Di-*o*-bromobenzoylhydrazine crystallises in white needles and melts at 245° . When heated with phosphoric oxide in a vacuum, it yields

di-o-bromophenyloxadiazole, $\begin{matrix} \text{N}:\text{C}(\text{C}_6\text{H}_4\text{Br}) \\ | \\ \text{N}:\text{C}(\text{C}_6\text{H}_4\text{Br}) \end{matrix} > \text{O}$, which crystallises in

leaflets, melts at 108° , and boils at $240\text{--}250^{\circ}$ under 13 mm. pressure. When heated with phosphorus pentasulphide at 200° in a vacuum, *s*-di-*o*-bromobenzoylhydrazine yields *di*-*o*-bromophenylthiodiazole, which crystallises from alcohol and melts at 117° .

s-Di-*m*-bromobenzoylhydrazine (Curtius and Portner, Abstr., 1899, i, 136) yields *di*-*m*-bromophenylloxadiazole, which crystallises in white, microscopic needles and melts at 179° , and *di*-*m*-bromophenylthiodiazole, which crystallises in delicate needles and melts at 175° .

s-Di-*p*-bromobenzoylhydrazine crystallises in leaflets and melts and decomposes at about 300° . It forms *di*-*p*-bromophenylloxadiazole, which crystallises in long needles and melts at 249° , and *di*-*p*-bromophenylthiodiazole, which crystallises from alcohol and melts at 237° .

G. Y.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. IX. Conversion of the Hydrazines of Propionic and isoValeric Acids into Heterocyclic Compounds. ROBERT STOLLE and HERMANN HILLE (*J. pr. Chem.*, 1904, [ii], 69, 481—485. Compare Abstr., 1902, i, 141).—*Diethylloxadiazole* is formed when *s*-dipropionylhydrazine is heated with phosphoric oxide or with propionic anhydride at 200° in a sealed tube; it boils at 198° under 760 mm. pressure, is miscible with water, alcohol, or ether, and gives a white precipitation with mercuric chloride.

Diethylthiodiazole, obtained by heating *s*-dipropionylhydrazine with phosphorus pentasulphide under reduced pressure, boils at 105° under 14 mm. pressure and is miscible with water, alcohol, or ether.

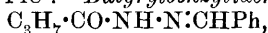
Diisobutyl-s-dihydrotetrazine, $\text{C}_4\text{H}_9\cdot\text{C}\begin{smallmatrix} \text{NH}\cdot\text{N} \\ \text{N}\cdot\text{NH} \end{smallmatrix}\text{C}\cdot\text{C}_4\text{H}_9$, is obtained in the preparation of *isovalerylhydrazide* from hydrazine hydrate and ethyl *isovalerate* (Hille, *loc. cit.*). It crystallises in plates and melts at 197° .

Diisobutylloxadiazole is obtained when ethyl *isovalerate* is heated with hydrazine hydrate in a sealed tube at $220\text{--}230^{\circ}$. It is a strongly refractive, colourless liquid, which boils at 140° under 17 mm. or at 232° under 760 mm. pressure. It is miscible with alcohol, ether, or much water and gives a white precipitation with mercuric chloride.

Diisobutylthiodiazole, formed by heating *s*-diisovalerylhydrazine with phosphorus pentasulphide, is a colourless liquid. It boils at $130\text{--}132^{\circ}$ under 25 mm. pressure and is miscible with alcohol or ether, but not with water.

G. Y.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. X. Conversion of the *n*-Butyryl Hydrazides into Heterocyclic Compounds. ROBERT STOLLÉ and GUSTAV ZINSSER (*J. pr. Chem.*, 1904, [ii], 69, 486—496).—*n*-Butyrylhydrazide, obtained together with a small amount of *s*-di-*n*-butyrylhydrazine when ethyl butyrate is boiled with hydrazine hydrate, crystallises in needles, melts at 44° , boils at 138° under 20 mm. pressure, is very hygroscopic, and reduces ammoniacal silver nitrate in the cold. The *hydrochloride*, $\text{C}_3\text{H}_7\cdot\text{CO}\cdot\text{N}_2\text{H}_3\cdot\text{HCl}$, is obtained as a white, crystalline powder which melts at 148° . *Butyrylbenzylidenehydrazide*,



crystallises in slender, yellow needles and melts at 98°. *n*-Butyryl-acetonehydrazide, $C_3H_7 \cdot CO \cdot NH \cdot N : CMe_2$, crystallises in glistening leaflets and melts at 82°.

3 : 6-Dipropyl-*s*-dihydropyridazine, $C_3H_7 \cdot C \begin{smallmatrix} \text{NH} \cdot \text{N} \\ \text{N} \cdot \text{NH} \end{smallmatrix} C \cdot C_3H_7$, is formed when butyrylhydrazide is heated in a sealed tube at 180°; it crystallises in leaflets, melts at 179°, is easily soluble in water, alcohol, or glacial acetic acid, and does not reduce ammoniacal silver solutions on warming.

s-Dibutyrylhydrazine and a small amount of dipropylloxadiazole are formed when hydrazine hydrate is heated with excess of ethyl butyrate in a sealed tube at 150°. *s*-Dibutyrylhydrazine is obtained in better yield by the action of butyric anhydride on hydrazine hydrate.

s-Di-*n*-butyrylhydrazine crystallises from alcohol, melts at 168°, boils at 214° under 24 mm. pressure, reduces ammoniacal silver solutions in presence of sodium hydroxide, and forms a copper compound, $(C_3H_7 \cdot CO)_2N_2Cu$ or $C_3H_7 \cdot CO \cdot NH \cdot N(Cu \cdot OH) \cdot CO \cdot C_3H_7$, as a green precipitate on addition of copper acetate to the aqueous solution.

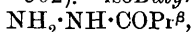
Dipropylloxadiazole, $CPra \begin{smallmatrix} \text{N} \cdot \text{N} \\ -O- \end{smallmatrix} CPr^a$, is formed when *n*-butyrylhydrazide is heated with excess of *n*-butyric anhydride at 150° under pressure. It is a colourless liquid which boils at 123° under 19 mm., or at 227° under atmospheric pressure, is miscible with water, alcohol, or ether, and forms a white emulsion with mercuric chloride in aqueous solution.

Dipropylthiodiazole, obtained by heating dibutyrylhydrazine with phosphorus pentasulphide, is a yellow liquid which boils at 127° under 13 mm. pressure, is easily soluble in alcohol, ether, or chloroform, and in concentrated aqueous solution gives white precipitates on addition of silver nitrate or mercuric chloride.

2 : 5-Dipropyl-1 : 3 : 4-triazole is formed when dibutyrylhydrazine is heated with ammonium zinc chloride at 250°, and is also obtained as a by-product from the preparation of dibutyrylhydrazine from ethyl butyrate and hydrazine hydrate, probably owing to intermediate formation of dipropyldihydropyridazine. Dipropyltriazole melts at 70°, boils at 177° under 16 mm. pressure, is hygroscopic, and forms a silver compound, $\begin{smallmatrix} \text{N} : CPr^a \\ \text{N} : CPr^a \end{smallmatrix} > NAg$.

G. Y.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. XI. Conversion of *iso*Butyric Acid into Heterocyclic Compounds. ROBERT STOLLÉ and LEO GUTMANN (*J. pr. Chem.*, 1904, [ii], 69, 497—502).—*iso*Butyrylhydrazide,



obtained by boiling ethyl *isobutyrate* with hydrazine hydrate, crystallises in glistening needles, melts at 104°, is easily soluble in alcohol or water, and reduces ammoniacal silver and Fehling's solutions. *iso*-Butyrylbenzylidenehydrazide crystallises in delicate, yellow needles and melts at 103°. *iso*Butyrylacetonehydrazide melts at 90—91°. 3 : 6-Di-*iso*-

propyl-s-dihydrotetrazine, $\text{CPr}^\beta \begin{smallmatrix} \text{NH} \cdot \text{N} \\ \diagup \quad \diagdown \\ \text{N} \cdot \text{NH} \end{smallmatrix} \text{CPr}^\beta$, formed when *isobutyrylhydrazide* is heated at 270° under pressure, crystallises in glistening leaflets and melts and decomposes at 221° .

Diisobutyrylhydrazine, $\text{COPr}^\beta \cdot \text{NH} \cdot \text{NH} \cdot \text{COPr}^\beta$, formed by the action of *isobutyric anhydride* on *hydrazine hydrate* in the cold, crystallises in white, matted needles, melts at 239° , and is easily soluble in hot alcohol. *Diisopropylloxadiazole*, prepared by the action of *isobutyric anhydride* on *diisobutyrylhydrazine* at 150° under pressure, boils at 209° and gives a white precipitate with mercuric chloride in aqueous solution. *2:5-Diisopropyl-1:3:4-triazole* forms a white, crystalline mass which melts at about $140-150^\circ$. With silver nitrate in ammoniacal alcoholic solution, it forms a *silver* compound, $\text{C}_8\text{H}_{14}\text{N}_3\text{Ag}$. *Diisopropylthiodiazole* is a liquid which boils at 126° under 27 mm. pressure, and forms white precipitates with mercuric chloride or silver nitrate in aqueous solution. G. Y.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. XII. Conversion of *s*-Dilaurylhydrazine into Diazole Derivatives. ROBERT STOLLÉ and CHRISTIAN SCHÄTZLEIN (*J. pr. Chem.*, 1904, [ii], 69, 503—505).—*Diundecyloxadiazole*, $\text{C}_{11}\text{H}_{23} \cdot \text{C} \begin{smallmatrix} \text{N} \cdot \text{N} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C} \cdot \text{C}_{11}\text{H}_{23}$, obtained by heating *s*-dilaurylhydrazine under reduced pressure, crystallises in feathery aggregates of needles, melts at 56° , boils at 275° under 22 mm. pressure, and is hydrolysed to dilaurylhydrazine when boiled with dilute sulphuric acid. *Diundecylthiodiazole*, formed when dilaurylhydrazine is heated with phosphorus pentasulphide, crystallises in feathery masses and melts at 49° . *2:5-Diundecyl-1:3:4-triazole* is formed when laurylhydrazide is heated under pressure at 300° , or when diundecyl-*s*-dihydrotetrazine is heated at 250° in a vacuum. It crystallises in small needles, melts at 89° , and forms a *silver* derivative with silver nitrate in alcoholic solution. G. Y.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. XIII. Dipentadecylfurodiazole and Dipentadecylthiodiazole. ROBERT STOLLÉ and F. H. DELLSCHAFT (*J. pr. Chem.*, 1904, [ii], 69, 506—508).—*Dipentadecyloxadiazole* is formed along with a substance which crystallises in flat, yellow needles and melts at 118° , when *s*-dipalmitylhydrazine is heated under reduced pressure. It separates from alcohol in feathery crystals, melts at 72° , and is hydrolysed by boiling dilute sulphuric acid, but not by dilute alcoholic sodium hydroxide, to *s*-dipalmitylhydrazine.

Dipentadecylthiodiazole, formed along with the substance melting at 118° when *s*-dipalmitylhydrazine is heated with phosphorus pentasulphide, melts at 60° . G. Y.

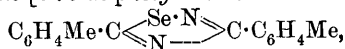
Formation of Heterocyclic Compounds from Hydrazine Derivatives. XIV. Selenodiazole. ROBERT STOLLE and LEO GUTMANN (*J. pr. Chem.*, 1904, [ii], 69, 509—512).—*Dimethylselenodiazole*, $\text{CMe} \begin{smallmatrix} \text{N} \cdot \text{N} \\ \diagup \quad \diagdown \\ \text{Se} \end{smallmatrix} \text{CMe}$, formed when *s*-diacetylhydrazine is heated

with phosphorus pentaselenide, melts at 77° , boils at 121° under 23 mm. pressure, dissolves in concentrated sulphuric acid to a green solution, and forms an *additive* compound, $C_4H_6N_2Se, AgNO_3$, with silver nitrate in alcoholic solution.

Diphenylselenodiazole, from *s*-dibenzoylhydrazine and phosphorus pentaselenide, crystallises in glistening scales, melts at 156° , is easily soluble in alcohol or ether, and does not react with dilute acids or alkalis, or with ammoniacal silver nitrate. G. Y.

Action of Hydrogen Selenide on Nitriles. W. BECKER and JULIUS MEYER (*Ber.*, 1904, 37, 2550—2555).—As stated by von Dechend (this Journal, 1875, 270), benzonitrile, in presence of a small quantity of alcoholic ammonia, is readily converted by hydrogen selenide into selenobenzamide, $CSePh \cdot NH_2$, which is transformed by iodine in alcoholic solution into *dibenzenyldiazoselenime* [3:5-diphenyl-1:2:4-selenodiazole], $CPh \begin{smallmatrix} \text{Se} \cdot \text{N} \\ \text{N} \end{smallmatrix} CPh$. This substance crystallises in long, white, silky needles, melts at 85° , and gives a *platinichloride*, $(C_{14}H_{10}N_2Se)_2, H_2PtCl_6$, separating in golden-yellow crystals; on reduction with alcoholic sodium, it gives benzylamine, but with zinc and hydrochloric acid the action is different, and a well-defined product could not be isolated. On this account, the substance seems to be similar to the dibenzenyldiazoximes and dibenzenyldiazosulphimes, and the alternative formula, $CPh \begin{smallmatrix} \text{N} \cdot \text{N} \\ \text{Se} \end{smallmatrix} CPh$, less probable than that given above.

p-Toluic selenoamide, $C_6H_4Me \cdot CSe \cdot NH_2$, prepared from *p*-toluonitrile and hydrogen selenide, crystallises from alcohol in beautiful, golden needles, melts at 161° , and is converted by iodine into *p*-dimethyl-dibenzenyldiazoselenime [3:5-di-*p*-tolyl-1:2:4-selenodiazole],



which crystallises from alcohol in white needles, melts at 116° , and gives a *platinichloride*, $(C_{16}H_{14}N_2Se)_2, H_2PtCl_6$. On reduction with alcoholic sodium, it gives *p*-tolylmethylamine, $C_6H_4Me \cdot CH_2 \cdot NH_2$, but with zinc and hydrochloric acid another substance, possibly tolenylamidine, $C_6H_4Me \cdot C(NH_2)_2 \cdot N \cdot CH_2 \cdot C_6H_4Me$, is produced.

Attempts to combine hydrogen selenide with aliphatic nitriles gave no issue. Similarly, experiments to condense thioacetamide, either with itself or with thiobenzamide, were fruitless. Hydrogen selenide does not combine with benzyl cyanide, but simply hydrolyses it to phenylacetic acid. W. A. D.

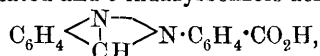
The Polyacid Salts of Rosaniline. JULES SCHMIDLIN (*Compt. rend.*, 1904, 138, 1508—1510).—The author has prepared the following triacid salts of the rosaniline series in a state of purity: rosaniline trihydrochloride, black crystals; pararosaniline trihydrochloride, black crystals; hexamethyl pararosaniline trihydrochloride, violet-black powder; all these salts dissolve in water or alcohol with the same colour as the corresponding mono-acid salts. Rosenstiehl described a magenta tetrahydrochloride obtained by saturating the base with

hydrogen chloride and removing the excess of acid by means of a current of air; the author finds that this method does not give a definite compound, the amount of hydrogen chloride absorbed increasing as the temperature decreases, thus a pentahydrochloride of a red colour is obtained at the ordinary temperature and pressure, but as the temperature is lowered more hydrogen chloride is absorbed and the compound becomes orange, until at -70° the colour is a pale yellow and the composition of the compound is intermediate between a hexa- and a hepta-hydrochloride, whilst at the temperature of liquid air hydrogen chloride is rapidly absorbed and the product is white.

M. A. W.

Transformation of Azo-compounds containing an Ortho-substituted Alcohol Radicle into Indazyl Derivatives. PAUL FREUNDLER (*Compt. rend.*, 1904, 138, 1276—1278).—Benzene-*o*-azobenzyl alcohol on distillation, or when warmed at 100° with dilute sulphuric acid, is converted by loss of H_2O into phenylindazole (compare Abstr., 1903, i, 585). In the cold, and even at 100° in alkaline, neutral, or only feebly acid solution, it is, on the other hand, relatively stable.

The two di-ortho-substituted azo-compounds, $\text{OH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ and $\text{N}_2(\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OH})_2$, are much less stable. In attempting to obtain the first of these from the methyl ester by the action of cold alcoholic soda, water is eliminated and *o*-indazylbenzoic acid,



formed; it melts at $204\text{--}205^{\circ}$. The second compound, *o*-azobenzyl alcohol decomposes spontaneously in the cold in acetone or alcohol solution, and *o*-indazylbenzyl alcohol is obtained melting at $56\text{--}57^{\circ}$ and distilling at 250° under 20—25 mm. pressure. The presence of a $\text{CH}_2\cdot\text{OH}$ or CO_2H group in the ortho-position in the second benzene nucleus thus facilitates in a high degree the formation of indazyl derivatives.

H. M. D.

Formation of Diazo-compounds. ANGELO ANGELI (*Ber.*, 1904, 37, 2390—2391. Compare Abstr., 1901, i, 322; 1902, i, 765).—The action of benzenesulphohydroxamic acid and phenylhydroxylamine on α -naphthol in alcoholic potassium hydroxide solution leads to the formation of benzeneazo- α -naphthol.

G. Y.

The Limit of Coupling of Diazobenzene with Phenol. LÉO VIGNON (*Compt. rend.*, 1904, 138, 1278—1280).—The author obtains *p*-hydroxyazobenzene in 80 per cent. yield by coupling one molecule of phenol with one molecule of diazobenzene chloride. By employing two molecules of the latter, an 80 per cent. yield of phenolbisdiazobenzene, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{N}_2\text{Ph})_2$, is obtained, in which the diazo-groups occupy the ortho- and para-position relatively to the OH group. It crystallises in reddish-brown spangles, melts at $123\text{--}124^{\circ}$, and is readily soluble in ether or light petroleum, less so in alcohol, insoluble in water, but

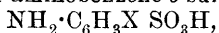
readily soluble in alkali hydroxides. Attempts to couple a third molecule of diazobenzene chloride with phenol have given no result. The formation of the bisdazo-compound thus appears to represent the limit of combination.

H. M. D.

Azo-dye from Anthranilic Acid and *p*-Cresol. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 151279).—Unlike other phenols, *p*-cresol, on combination with diazotised anthranilic acid, yields a reddish-yellow dye which gives a dark claret colour when mordanted with chromium salts.

C. H. D.

[Azo-compounds from 2-Hydroxy-3-naphthoic Acid.] AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 151205).—Para-substituted derivatives of aminobenzene-*o*-sulphonic acid,



in which X = CH₃, C₂H₅, NO₂, Cl, Br, or OMe, form soluble diazonium compounds which combine with 2-hydroxy-3-naphthoic acid to form red dyes. The sparingly soluble sodium salts of these dyes are readily converted into metallic lakes, which are very fast towards light.

C. H. D.

[Benzorhodamines. Basic Dyes of the Triphenylmethane Series.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 150440).—Benzorhodamines are obtained by the condensation of benzaldehyde or its derivatives with monoalkyl derivatives of *o*-amino-*p*-cresol, conversion into pyrone derivatives, and oxidation. Thus, *o*-chlorobenzaldehyde condenses with *o*-methylanino-*p*-cresol sulphate to form the sulphate of a new base, crystallising in colourless needles. On heating with sulphuric acid or zinc chloride and adding alkali hydroxide, the *pyrone* is obtained as a red, crystalline mass. Ferric chloride oxidises it to the *benzorhodamine*, which forms red, felted needles, dissolving in water to a red solution with yellow fluorescence. Similar dyes are obtained from other substituted benzaldehydes.

C. H. D.

Yellow Dyes of the Acridine Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 151206).—Diaminoacridine derivatives, such as acridine-yellow and benzoflavin, are converted into new orange-yellow dyes by heating with twice their weight of glycerol for several hours at 150—180°. The hydrochlorides of the leuco-bases may also be employed. The new dyes, the nature of which is not yet determined, form reddish-brown powders dissolving readily in water. The solutions in concentrated sulphuric acid are brown, becoming green on warming.

C. H. D.

Trisazo-dyes from 2:4-Diaminoacetanilide. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 151204).—2:4-Diaminoacetanilide, prepared by reduction of 2:4-dinitroacetanilide, melts at 158—159° and dissolves readily in water, sparingly in alcohol or benzene. Black trisazo-dyes are obtained by diazotising acetyl-*p*-phenylenediamine, combining with 7-amino-*a*-naphthol-3-sulphonic acid.

removing the acetyl group, preparing the tetrazo-compound, and combining with 2 mols. of the new base, or with 1 mol. of the new base and 1 mol. of a suitable diamine. C. H. D.

Fatty-aromatic Diazoamino-compounds (Triazens). LUDWIG WOLFF and HANS LINDENHAYN (*Ber.*, 1904, 37, 2374—2381).—*β*-Cyano-*α*-phenyltriazen (benzazocyanamide), $C_6H_5 \cdot N:N \cdot NH \cdot CN$, forms colourless flakes, which soon become yellow, melts at 72° with vigorous "puffing," and can be exploded by a blow or by contact with sulphuric acid. The *potassium* derivative, $C_7H_5N_4K \cdot H_2O$, from which the cyanide was separated, was prepared by the action of potassium cyanide on diazobenzimide, $C_6H_5 \cdot N_3$; it forms colourless, silvery flakes, dissolves readily in water to an alkaline solution, and less readily in cold alcohol. The *silver*, *iron*, and *copper* derivatives are insoluble; the *barium* salt crystallises in broad, colourless needles. Reduction with zinc dust and ammonia gives phenylhydrazine; concentrated hydrochloric acid gives diazobenzene chloride and carbamide, whilst 10 per cent. potassium hydroxide gives ammonia, carbon dioxide, and aniline, but not phenol.

α-Cyano-*β*-phenyl-*β*-methyltriazen [methylanilinoazo cyanide],
 $NMePh \cdot N:N \cdot CN$,

prepared by the action of methyl iodide on the potassium salt, crystallises from hot alcohol in nearly colourless flakes, melts at 69 — 70° , and dissolves in concentrated hydrochloric acid, but is reprecipitated by water. Aqueous sodium hydroxide decomposes it very rapidly at 60 — 70° , giving methylaniline, nitrogen, and sodium cyanate, whilst concentrated hydrochloric acid gives ammonia and methylaniline.

α-Phenyltriazen-*β*-thiocarbamide, $NPh \cdot N:N \cdot NH \cdot CS \cdot NH_2$, prepared by the action of ammonia and hydrogen sulphide on the potassium derivative, crystallises from hot alcohol or chloroform in nearly colourless, glistening flakes or needles and decomposes at 110 — 111° with liberation of gas; it is very stable towards hot sodium hydroxide, but is decomposed by cold hydrochloric acid, giving diazobenzene and thiocarbamide. The *methyl* derivative, $NMePh \cdot N:N \cdot CS \cdot NH_2$, crystallises from hot alcohol in yellowish-red needles, detonates at 97° , and is decomposed by hydrochloric acid with gradual liberation of nitrogen.

T. M. L.

Chemical Nature of Histon and the Proteids from which it is Extracted. CARLO FOA (*Atti R. Accad. Lincei*, 1904, 13, i, 414—422).—The author gives, in a tabulated form, the principal reactions, some of which are new, of histon, acid albumin, proto-albumose, deuto-albumose, hetero-albumose, peptone, and ovo-protein. It is seen from this that histon has many reactions in common with acid-albumin, the proteoses, and peptones. When subjected to pepto-hydrochloric digestion for 48 hours, histon is transformed partly into proteoses and partly into peptones. Histon is formed by the action of dilute hydrochloric acid on the stroma of anucleated red corpuscles.

T. H. P.

Salmin and Clupein. ALBRECHT KOSSEL and HENRY D. DAKIN (*Zeit. physiol. Chem.*, 1904, 41, 407—415. Compare this vol., i, 211, 355, and Abderhalden, *ibid.*, i, 463).—Further researches by the aid of Fischer's esterification method indicate the absence of alanine and leucine among the products of the hydrolysis of salmin.

The following numbers give the amounts of the various hydrolytic products obtained when the amount of salmin = 100. Arginine, 87.4; serine, 7.8; aminovaleric acid, 4.3; and pyrrolidine-2-carboxylic acid, 11.0.

The products obtained from clupein are arginine, aminovaleric acid, serine, alanine, and pyrrolidine-2-carboxylic acid. J. J. S.

Action of 4 per cent. Sulphuric Acid on Legumin. DMITRI PRIANISCHNIKOFF (*Landw. Versuchs-stat.*, 1904, 60, 27—40).—Legumin is quickly decomposed by 4 per cent. sulphuric acid when heated, being converted into substances which are not precipitated by copper hydroxide. At the commencement, compounds are produced which are not precipitated by phosphotungstic acid, and after prolonged heating as much as two-thirds of the total nitrogen is in this form. It is probable that amino-acids are formed. Nitrogen as ammonia and as hexon bases also increase during the treatment, and represent finally a tenth and a fifth respectively of the total.

Peptones are produced at first in considerable quantity, but as the heating is continued are decomposed. N. H. J. M.

Action of Heat and Acidity on Amylase. PAUL PETIT (*Compt. rend.*, 1904, 138, 1231—1233. Compare this vol., i, 541).—The liquefying and saccharifying activity of a slightly alkaline infusion of malt is increased by the addition of small quantities of lactic acid; at one stage of the addition a precipitate appears which increases at first with the acidity and then redissolves. The precipitate can be filtered, washed and dried; it acquires a brown colour, and when once dry does not dissolve readily in dilute acid or alkalis, whilst the filtrate gives the Schoenbein reaction, and liquefies and saccharifies starch paste. In a series of experiments, equal quantities of malt infusion neutralised with *N*/50 sodium carbonate were acidified with varying quantities of *N*/50 lactic acid, heated for 10 minutes in a water-bath, cooled and neutralised with *N*/50 sodium carbonate; the results showed that a quantity of acid had disappeared, the amount increasing with the initial acidity of the solution; thus if x denote the initial quantity of acid and y the variation in the acidity, $y = 0.4 - 0.337x$. The author assumes that the amylase displaced from an insoluble lactonic combination by means of the sodium carbonate forms a compound with the acid which is soluble in small quantities of acid, but is precipitated when the quantity of acid reaches a certain limit. M. A. W.

Hydrolysis of Ethyl Butyrate by Lipase. JOSEPH H. KASTLE, MARIUS EARLY JOHNSTON, and ELIAS ELVOVE (*Amer. Chem. J.*, 1904, 31, 521—550).—It has been shown by Kastle and Loevenhart (*Abstr.*, 1901, i, 178) that the activity of lipase solutions is greatly diminished by filtration, and this conclusion has now been confirmed by further

experiments. A solution of lipase was prepared by extracting fresh hog liver with water, and adding a small quantity of *N*/100 hydrochloric acid to the aqueous extract; the mixture was then heated to 40°, when a heavy, albuminous precipitate was produced. On filtering, a clear solution was obtained, the activity of which towards ethyl butyrate was not much more than one-half of that of the unfiltered extract. The residue left on filtration was found to be comparatively insoluble in water but readily soluble in 0.2 per cent. solution of sodium carbonate. This alkaline lipase solution is very active towards ethyl butyrate, but during hydrolysis gives rise to a heavy precipitate of coagulated proteid. This precipitate is not formed with clear solutions of the ferment prepared with very dilute acids (preferably butyric acid), and the latter were therefore used in the further study of the action of the enzyme on ethyl butyrate.

Clear solutions of lipase containing small quantities of hydrochloric or butyric acid are very stable, and can be kept for several weeks without showing any considerable decrease in lipolytic activity. They may be repeatedly filtered through paper without any loss of activity, but on filtration through a porous cup, the enzyme is completely removed and the solution rendered inactive.

A large number of experiments have been carried out with a view of determining the coefficient of velocity of the hydrolysis of ethyl butyrate by lipase under slightly varying conditions of concentration, temperature, and time. The velocity of the reaction during the first interval of 15 minutes is greatly diminished by the presence of free hydrochloric or butyric acid, but the coefficients of velocity during the succeeding intervals are practically the same in all cases, showing that the effect of these small quantities of acid on the enzyme is only temporary. Small amounts of free acids retard the action of the enzyme, but do not permanently impair its activity, whilst large quantities of acids completely destroy the ferment.

The nature of the hydrolytic change was investigated by van't Hoff's method, which depends on the effect of change of concentration on the velocity of the reaction. It was found that it is a unimolecular process which is influenced to a small extent by the acid produced in the hydrolysis. Alcohol slightly retards the action of the enzyme, but the quantities produced in the hydrolysis of dilute solutions are so small that their effect is negligible.

The velocity constants have been determined at 0°, 10°, 20°, 30°, and 40°, and found to increase considerably with rise of temperature. The average ratio of the velocities between one temperature and another 10° higher is as 1 : 1.69.

Lipase, whilst effecting the hydrolysis of ethyl butyrate, suffers no permanent alteration, but retains its activity unimpaired. The amount of ethyl butyrate hydrolysed by lipase is, within certain limits, independent of the concentration of the ester.

The comparative activity of lipase, hydrochloric acid, and sodium hydroxide towards ethyl butyrate was studied. The concentration of the lipase solution was determined by evaporating a portion of it to dryness at 110° and weighing the residue. It is not improbable that only a small proportion of this residue consists of the enzyme, but for

the purpose of comparison it was regarded as pure lipase. The results indicate that the power of lipase to hydrolyse ethyl butyrate in dilute solution is far greater than that of either sodium hydroxide or hydrochloric acid, but that the action of the enzyme on the ester more nearly resembles that of sodium hydroxide than that of hydrochloric acid. E. G.

Oxidising Ferments. ROBERT CHODAT and ALEXIS BACH (*Arch. Sci. phys. nat.*, 1904, [iv], 17, 477—510. Compare Abstr., 1902, ii, 344; 1903, i, 219; and this vol. i, 359).—Two classes of substances are concerned in biological oxidations. Peroxides of the type $\text{HO}\cdot\text{OH}$, in which the hydrogen is replaced, or partially replaced, by an inorganic or organic radicle, having the characters of a ferment. These the authors designate *oxygenases*. The other class consists of peroxydases, ferments which render peroxides active in a manner similar to the effect of hydrolytic ferments on water.

Catalase is not a true oxidising ferment, being neither a peroxide of the oxygenase type nor a ferment which renders active free or combined oxygen. Its only function is the decomposition of hydrogen peroxide.

Up to the present time, it has only been possible to oxidise the hydrogen of phenols, aldehydes, aromatic amines, and hydriodic acid. In the case of *o*-phenylenediamine, a simple condensation to diamino-phenazine takes place (compare Ullmann, Abstr., 1903, i, 199). Many substances which occur in plants, such as arbutin, æsculin, and tannin, are readily oxidised by the same agents, and it is not impossible that the condensations of polysaccharides and alkaloids, &c., are due to similar oxidations. N. H. J. M.

Non-existence of Philothion, a Supposed Sulphur-reducing Enzyme. J. E. ABELOUS and H. RIBAUT (*Bull. Soc. chim.*, 1904, [iii], 31, 698—701. Compare Pozzi-Escot, Abstr., 1902, i, 513, 580, 654, 655, 577; ii, 635; 1903, i, 670; this vol., i, 130; ii, 272. Rey Pailhade, Abstr., 1881, 1101; 1896, ii, 326; 1900, ii, 678. Abelous and Gerard, Abstr., 1900, ii, 226; Abelous and Aloy, this vol., ii, 188, and Loew, Abstr., 1901, i, 435).—The authors find that extracts prepared by maceration of the liver of the horse, or of beer yeast in water saturated with chloroform, possess even after ebullition for some minutes the property of producing hydrogen sulphide on the addition of sulphur. Further, the rate at which hydrogen sulphide is evolved from solutions containing albumin, yeast extract, and liver extract, on addition of sulphur, increases steadily with rise of temperature, and exhibits no optimum temperature below 125° , the maximum at which observations were made. They are of opinion, therefore, that Pozzi-Escot's assertion that the formation of hydrogen sulphide under these conditions is due to the activity of a reducing enzyme is unjustifiable. T. A. H.

Organic Chemistry.

Electrolytic Preparation of Bromoform. ERICH MÜLLER and RICHARD LOEBE (*Zeit. Elektrochem.*, 1904, 10, 409—414).—The authors have modified the method of preparation of bromoform described by Coughlin (*Abstr.*, 1902, i, 197) by omitting the diaphragm. In order to avoid reduction of the acetone or of the products of the reaction, it is necessary to add potassium chromate to the solution. In order to get a good current efficiency, it is necessary to arrange the experiment so that a mixture of bromine and bromoform is produced; this is finally shaken with a solution of acetone and sodium carbonate until it is colourless; the current efficiency is then over 90 per cent. The conditions required are: a solution containing about 25 per cent. of potassium bromide, 12.5 per cent. by volume of acetone, and 0.2 per cent. of potassium chromate; current density at the platinum anode, 0.07 ampere per sq. cm. The bromoform is kept well mixed with the liquid and the alcohol-hydroxide formed is neutralised by a rapid current of carbon dioxide. T. E.

Addition of Hydrogen Haloids to Olefines in Acetic Acid and Aqueous Solutions. II. WLADIMIR N. IPATIEFF and W. N. DECHANOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 659—669).—In presence of acetic acid, ethylenic hydrocarbons combine readily with hydrogen bromide or iodide, but only slowly with hydrogen chloride. With hydrogen chloride and iodide, this combination always takes place according to the rule discovered by Markownikoff, but with hydrogen bromide a certain amount of abnormal product is always obtained. The proportion of abnormal product formed is different for different ethylenic hydrocarbons and becomes less as the difference between the amounts of hydrogen united with the carbon atoms on either side of the double linking increases. Thus, with *isobutylene*, containing the complex $\cdot\text{C}:\text{CH}_2$, the proportion of abnormal product is 6—7 per cent.; with *trimethylethylene*, containing $\text{C}:\text{CH}\cdot$, 10—15 per cent.; and with *isopropylethylene*, containing $\cdot\text{CH}:\text{CH}_2$, 50 per cent. T. H. P.

Synthesis in the Amylene Series; $\alpha\epsilon$ -Diamyloxyamylene $(\text{CH}_2)_5(\text{O}\cdot\text{C}_5\text{H}_{11})_2$, $\alpha\epsilon$ -Dibromoamylene, and $\alpha\epsilon$ -Di-iodoamylene. JULES HAMONET (*Compt. rend.*, 1904, 138, 1609—1612. Compare this vol., i, 467).— $\alpha\epsilon$ -Diamyloxyamylene, $\text{C}_5\text{H}_{10}(\text{O}\cdot\text{C}_5\text{H}_{11})_2$, prepared by the action of amyloxybromomethane on the magnesium derivative of δ -bromo- α -amyloxybutane, is a mobile liquid boiling at 159—160° under 20 mm. or at 276—277° under 759 mm. pressure, has a sp. gr. 0.844 at 18°, and reacts energetically with hydrogen bromide to form ϵ -bromo- α -amyloxyamylene, $\text{C}_5\text{H}_{11}\cdot\text{O}\cdot[\text{CH}_2]_4\cdot\text{CH}_2\text{Br}$, a liquid boiling at 130—131° under 20 mm. pressure, not crystallising in a mixture of solid carbon dioxide and ether, and yielding a magnesium derivative, $\text{C}_5\text{H}_{11}\cdot\text{O}\cdot\text{C}_5\text{H}_{10}\cdot\text{MgBr}$.

αα-Dibromoamylene, $C_5H_{10}Br_2$, prepared by the action of hydrogen bromide on *αα*-diamyloxyamylene at 100° in sealed tubes, is a liquid at the ordinary temperature, crystallises in a mixture of solid carbon dioxide and ether, the crystals melting at -34 to -35° ; it boils at 111 – 112° under 20 mm. or at 221° under 763 mm. pressure, and has a sp. gr. 1.706 at 18° . The dibromoamylene prepared by Gustavson and Demjanoff (compare Abstr., 1889, 950) from pentamethylenediamine and boiling at 208 – 214° under the ordinary pressure is probably not the *αα*-compound. *αα-Di-iodoamylene*, $C_5H_{10}I_2$, prepared in similar manner to the dibromo-compound, is a faintly colourless liquid boiling at 149° under 20 mm. pressure, having a sp. gr. 2.194 at 18° , and when cooled in a mixture of ice and salt, forming crystals which melt at 9° .

M. A. W.

Formation of Dimethylisopropylcarbinol in the Hydrogenation of Acetone. GEORGES DENIGES (*Compt. rend.*, 1904, 138, 1607–1609).—In addition to isopropyl alcohol and pinacone, dimethylisopropylcarbinol is also produced in the reduction of acetone by means of sodium according to the equation $2COMe_2 + 4H = CHMe_2 \cdot CMe_2 \cdot OH + H_2O$. In order to isolate the tertiary alcohol, which is formed only in small quantities, the reduction is effected at 0° in the presence of a saturated solution of potassium carbonate, the product washed with water, extracted with ether, and distilled. It passes over between 115° and 125° and is identical with the alcohol obtained by Grignard's synthesis from acetone and magnesium isopropyl bromide, or by Butleroff's method from zinc methyl and isobutyl chloride. It gives an orange precipitate, $(SO_4 \cdot \begin{smallmatrix} Hg \\ \text{---} \\ Hg \end{smallmatrix} O)_3 C_6H_{12}$, on boiling with an acid solution of mercuric sulphate, and a red explosive precipitate with mercuric nitrate (compare Abstr., 1900, i, 89) characteristic of tertiary alcohols.

Preliminary experiments seem to show that the production of a tertiary alcohol of twice the carbon content, in addition to a pinacone and a secondary alcohol of the same carbon content, is a general reaction in the hydrogenation of ketones of the paraffin series.

M. A. W.

A New Class of Ether Oxides. MARCEL DESCUDÉ (*Compt. rend.*, 1904, 138, 1703–1705).—*Diethoxymethyl oxide* [*diethoxymethyl ether*], $O(CH_2 \cdot OEt)_2$, prepared, together with diethoxymethane, by the action of sodium ethoxide on dichloromethyl oxide (compare this vol., i, 546), is a colourless, mobile liquid with an ethereal odour, boils at 140° , has a sp. gr. 0.90781 at $25^\circ/4^\circ$, n_D 1.38732, is soluble in the ordinary organic solvents, dissolves in ten times its weight of water, is decomposed by acids to form methanal and alcohol, and is not attacked by aqueous solutions of sodium or potassium carbonate. The molecular weight has been determined by the vapour density method, and also by the cryoscopic method in benzene or water. In view of these facts, the author concludes that the compound boiling at 102 – 106° , and having sp. gr. 0.864, obtained by Coops (compare Abstr., 1902, i, 77) by the action of alcohol on the product of the

reaction between hydrogen chloride and methanal is not diethoxy-methyl oxide

Dimethoxymethyl oxide, obtained similarly to the preceding compound, boils at 106–108°, has a sp. gr. 0.959 at 20°/20°, and forms a detonating mixture with oxygen at a red heat.

Corresponding derivatives of the higher alcohols could not be isolated owing to the decomposition which occurred on distilling the product of the reaction between dichloromethyl oxide and the sodium derivative of the alcohol. M. A. W.

Mixed Organo-inorganic Anhydrides. LUIGI FRANCESCONI and U. CIALDEA (*Gazzetta*, 1904, 34, i, 435–446).—The authors describe the methods and apparatus used in the preparation and analysis of mixed nitroso-organic anhydrides obtained by the action of nitrosyl chloride on the silver salts of organic acids (Abstr., 1903, i, 788). The anhydrides are best purified by distillation in a stream of dry carbon dioxide; they are explosive, and hence difficult to analyse.

Nitrosyl propionate, $\text{COEt}\cdot\text{O}\cdot\text{NO}$, resembles nitrosyl acetate (*loc. cit.*) in physical and chemical properties. It has the normal vapour density, and decomposes rapidly in the light, yielding propionic and nitrous anhydrides and becoming green.

Nitrosyl benzoate, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{O}\cdot\text{NO}$, is a yellow oil, very unstable towards light or heat; it readily absorbs moisture from the air, giving benzoic and nitrous acids. T. H. P.

Action of Hydrogen Peroxide on Anhydrides and the Formation of Organic Acid, Peroxides, and Peracids. ALPHONSO M. CLOVER and A. C. HOUGHTON (*Amer. Chem. J.*, 1904, 32, 43–68. Compare Clover and Richmond, Abstr., 1903, i, 396).—When acetic peroxide is dissolved in an aqueous solution of hydrogen peroxide, peracetic acid is produced at the expense of the active oxygen of the hydrogen peroxide; the amount produced is greater than that which would be formed in the ordinary hydrolysis of an aqueous solution of acetic peroxide, and its formation takes place much more rapidly than in the latter case.

If acetic anhydride is dissolved in hydrogen peroxide solution, both peracetic acid and acetic peroxide are produced. A study of the rate of formation of these two substances shows that the peracetic acid is formed first, and that the peroxide is produced by the action of the peracetic acid on the anhydride. The action of hydrogen peroxide on acetic anhydride is much more rapid than that of water.

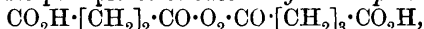
Propionic anhydride behaves towards hydrogen peroxide in the same way as acetic anhydride.

When an excess of succinic anhydride is added to a solution of hydrogen peroxide, a crystalline precipitate of *succinic peroxide acid*, $[\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O}]_2$, is produced, which is moderately soluble in water, alcohol, acetone, or ethyl acetate, and sparingly so in ether. This compound is colourless and odourless, crystallises in irregular flat plates, softens at 115°, melts and decomposes at 128°, and does not explode on percussion. Its production is due to the action of the persuccinic acid first formed on the succinic anhydride present. The

aqueous solution of succinic peroxide acid gradually undergoes hydrolysis with the formation of persuccinic and succinic acids. It causes the rapid liberation of iodine from potassium iodide, and oxidises a managanous salt to permanganic acid. When the peroxide acid is heated with boiling xylene, it undergoes decomposition with the formation of carbon dioxide, succinic anhydride, succinic acid, adipic acid, and a gummy acidic substance.

Persuccinic acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, separates in large crystals from a mixture of chloroform and ether, melts and decomposes at 107° , and is soluble in water, alcohol, acetone, or ethyl acetate. When slowly heated, it undergoes decomposition with the formation of carbon dioxide and acrylic acid.

When a solution of persuccinic acid is treated with glutaric anhydride, a crystalline precipitate of *succinic glutaric peroxide acid*,



is produced, which softens at 105° , melts and decomposes at 107° , is readily soluble in alcohol, acetone, or ethyl acetate, and sparingly so in ether, and has a less powerful oxidising action than succinic peroxide acid.

Glutaric peroxide acid, $[\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O}]_2$, obtained by the action of hydrogen peroxide on glutaric anhydride, is a crystalline substance which melts and decomposes at 108° , is freely soluble in alcohol, acetone, or ethyl acetate, and moderately so in benzene. When heated with boiling xylene, it undergoes decomposition with the formation of carbon dioxide and suberic acid. E. G.

Behaviour of Cyanogen towards Methylene Compounds. WILHELM TRAUBE (*Annalen*, 1904, 332, 104—158).—The addition of cyanogen to methylene compounds takes place in the presence of traces of sodium ethoxide; when the temperature is kept low, 1 mol. of cyanogen reacts with 1 mol. of the methylene compound, but when no cooling agent is employed, with 2 mols. Thus, ethyl acetoacetate yields ethyl cyanoiminoethylacetoacetate, or ethyl dicyanoacetoacetate, $\text{CN}\cdot\text{C}(\text{:NH})\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$, which exists in 2 or 3 isomeric forms, and combines with a second mol. of the ester to form a di-imino-compound (compare Abstr., 1898, i, 241, and 1899, i, 192). Acids react immediately with the substance first mentioned, alcohol being eliminated and a deep yellow substance produced, which is now represented by the formula $\frac{\text{CHAc}\cdot\text{CO}}{\text{C}(\text{CN})\text{:N}}$, and is therefore the

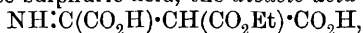
anhydride (lactam) of the imino-acid (compare *loc. cit.*). This compound is also formed when the ethyl dicyanoacetoacetate is added to an alcoholic solution of ethyl sodioacetoacetate. Ethyl dicyanodimalonate, formed from cyanogen and 2 mols. of ethyl malonate, loses 2 mols. of alcohol under the influence of alkalis, the anhydride (lactam) thus produced being very stable. That these compounds are anhydrides and not cyclopentene derivatives, as previously thought, is shown by the fact that under the influence of alkali hydroxides they yield acids containing nitrogen.

The di-imino-compounds, containing carbethoxy-groups, and other di-imino-compounds, as tetra acetyl-di-iminobutane and dicyanodiacetyl-

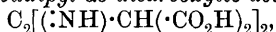
acetone, yield cyclic compounds with elimination of water. These appear not to be pentene derivatives, as previously believed, but pyrrole derivatives with a tertiary nitrogen atom.

When two methylene compounds combine with 1 mol. of cyanogen, two different di-imino-compounds are formed, according to the order in which the methylene compounds are combined with the cyanogen; thus, ethyl dicyanoacetate and ethyl malonate form a colourless additive product, but ethyl dicyanomalonate and ethyl acetoacetate form a yellow anhydride (lactam) with elimination of alcohol.

Action of Cyanogen on Ethyl Malonate [With C. HOEPNER.]—*Ethyl dicyanomalonate* (*ethyl cyanoiminoisosuccinate*), $C_9H_{12}O_4N_2$, is prepared by leading cyanogen into a well-cooled alcoholic solution of ethyl malonate containing a trace of sodium ethoxide, and forms crystals melting at 93° . If a solution of the ester in a concentrated alcoholic solution of ammonia is kept for 24 hours, *ethyl β -dicyanomalonate* separates in white needles melting at 123° . On treating the ester in alcoholic solution with hydrochloric or sulphuric acids, it is hydrolysed to the *acid ester*, $CN \cdot C(:NH) \cdot CH(CO_2Et) \cdot CO_2H$, which melts at 238° . When this compound is carefully heated at 100° with an aqueous solution of 2 mols. of sodium hydroxide and the liquid subsequently acidified with dilute sulphuric acid, the *dibasic acid ester*,



is obtained as colourless needles melting with evolution of carbon dioxide at 134° . The *sodium salt* forms leaflets. On reducing the dicyano-ester with 3 per cent. sodium amalgam in the presence of water, an *asparagine derivative*, $NH_2 \cdot CO \cdot CH(NH_2) \cdot CH(CO_2H)_2$, is formed, which crystallises out on addition of acetic acid; it melts and decomposes at 120° . The *dilactam* of ethyl dicyanodimalonate (*$\beta\gamma$ -di-imino-adipyl- $\alpha\delta$ -dicarbethoxydilactam*) is obtained by prolonged treatment of a solution of ethyl malonate in ethyl alcohol containing sodium ethoxide with cyanogen, and subsequent decomposition of the red sodium salt which separates with acids (compare Abstr., 1903, i, 76); the *disodium salt* crystallises in red crystals with $2H_2O$; the *potassium salt* forms purple-red crystals with $2H_2O$. When boiled with alkalis, hydrolysis takes place, *$\beta\gamma$ -di-iminoadipyl- $\alpha\delta$ -dicarboxylic acid*,



being formed as yellow needles (compare *loc. cit.*). A *dimethyl derivative* of the foregoing dilactam is obtained by treatment of the sodium salt in the presence of alcohol with methyl iodide; it crystallises in deep yellow needles melting at 150° ; the corresponding *ethyl compound* crystallises in yellow needles melting at 156° ; both these compounds react violently with ammonia, yielding diamino-compounds.

The *lactam* of ethyl dicyanomalonacetate, $C_{13}H_{16}O_6N_2$, is prepared by adding to a solution of ethyl dicyanomalonate a solution in alcohol of ethyl acetoacetate containing sodium ethoxide; on acidification, the ester separates and crystallises; it forms yellow needles, beginning to melt at 103° and is completely molten at 137° . The corresponding *methyl derivative*, $C_{14}H_{16}O_6N_2$, is obtained by using ethyl sodiomethylacetoacetate, and crystallises in yellow needles melting at 139° . The corresponding *benzoyl derivative*, $C_{18}H_{18}O_6N_2$, is similarly prepared from ethyl sodiobenzoylacetoacetate and forms

yellow needles melting at 194° . The lactam of ethyl dicyanomalonacetosuccinate, $C_{17}H_{22}O_8N_2$, is prepared from ethyl acetosuccinate and ethyl dicyanomalonate, and forms yellow crystals melting at 116° . Ethyl dicyanomalonate and acetylacetone condense in a similar manner in the presence of sodium ethoxide, forming the lactam, $C_{12}H_{14}O_5N_2$, which crystallises in dark yellow needles melting at 135° .

All attempts to hydrolyse these lactams by means of alkalis did not result in crystalline compounds, the action of aqueous hydrochloric acid led to the production of the di-imino-compounds, which, in their turn, were decomposed into a methylene compound and the cyanoimino-compound, ethyl dicyanomalonate.

Action of Cyanogen on Ethyl Acetoacetate and Acetylacetone [With M. BRAUMANN.]—When ethyl α -dicyanoacetoacetate is dissolved in alcoholic ammonia, an *amidine*, $C_8H_{13}O_3N_3$, separates after long keeping, which forms yellowish-white crystals decomposing at 209 – 211° , and is an additive product of ammonia and ethyl dicyanoacetoacetate in mol. proportions. On warming ethyl α -dicyanoacetoacetate with acidified water to 60° , ethyl α -acetyl- α' -iminosuccinamate, $C_8H_{12}O_4N_2$, is produced by addition of water; it crystallises in leaflets melting at 142° . On treating the ester last mentioned with sodium hydroxide

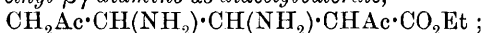
(1 mol.), acetylminosuccinimide, $\begin{array}{c} C(NH) \cdot CO \\ | \\ CHAc - CO \end{array} > NH$, is produced on

acidification in the form of plates which do not melt sharply. Its methyl derivative, $C_7H_8O_3N_2$, prepared by treating it in alcoholic solution with methyl iodide and sodium ethoxide, forms small, yellow crystals melting at 226 – 227° .

Ethyl β -dicyanoacetoacetate is obtained from the α -compound either by dissolving it in warm acetic acid and precipitating with water after cooling, or by dissolving in warm alcohol and passing in hydrogen chloride; this substance crystallises in rhombic plates melting at 178° , and combines with ammonia, not as does the isomeride, in mol. proportions, but in the proportion of 2 mols. of ester to 1 mol. of ammonia, 1 mol. of alcohol being eliminated, and the compound $C_{14}H_{17}O_5N_5$, which is crystalline and melts at 219° , being formed. Ethyl γ -dicyanoacetoacetate is prepared by treating the α -compound in alcoholic solution with ethylaniline or other secondary bases; it forms colourless crystals melting at 211° . Whilst the α -ester is decomposed with the formation of hydrocyanic acid and the β -ester remains unchanged when treated with methyl iodide and sodium ethoxide in alcoholic solution, the γ -ester yields ethyl dicyanomethylacetoacetate, $C_9H_{12}O_3N_2$, which crystallises in colourless needles melting at 110 – 113° .

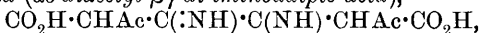
Ethyl β -dicyanodiacetoacetate is obtained from the ordinary ethyl dicyanodiacetoacetate (ethyl $\alpha\delta$ -diacetyl- $\beta\gamma$ -di-iminoadipate) by the action of sodium amalgam; the oily reduced product is removed by ether, and the alkaline liquor acidified, when the β -compound separates in colourless needles melting at 132.5° ; it gives no coloration either with sulphuric or hydrochloric acid or with ferric chloride, whilst the α -ester yields respectively a purple-red, a dirty-green and a wine-red coloration with these reagents. The α -ester is dissolved by alkali hydroxides with a yellowish-red coloration, alcohol being eliminated and the lactam produced, which is precipitated on acidifying. The

β -ester, on the other hand, forms a colourless solution in alkalis and is reprecipitated unchanged by acids. The reduced product previously mentioned is *ethyl $\beta\gamma$ -diamino- $\alpha\delta$ -diacetylvalerate*,

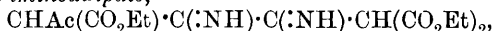


it forms colourless needles melting at 35° , and has marked basic properties.

The *lactam*, prepared from ethyl dicyanodiacetoacetate by the regulated action of alkalis, forms dark yellow needles melting at 136° , and dissolves in alkali hydroxide unchanged, forming a reddish yellow solution which decomposes on keeping. When the lactam is heated with a solution of 8 per cent. sodium hydroxide (6 mols.), *dicyanodi-acetoacetic acid* (*$\alpha\delta$ -diacetyl- $\beta\gamma$ -di-iminoadipic acid*),



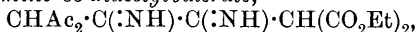
separates in colourless needles on acidification, and melts with evolution of carbon dioxide at 230° . A study of the nearly allied *ethyl α -carboxy- δ -acetyl- $\beta\gamma$ -di-iminoadipate*,



shows that this compound is not converted into a lactam by alkalis, but is partly hydrolysed into an *ester acid*, $\text{C}_{13}\text{H}_{18}\text{O}_7\text{N}_2$, which contains one carboxy-group, is crystalline, and melts at 160° . Attempts to eliminate the nitrogen from this ester failed. Hydrochloric acid was without action; when the ester was simultaneously treated with nitrous and hydrochloric acids, half the nitrogen was eliminated, but instead of the expected compound $\text{C}_{15}\text{H}_{21}\text{O}_8\text{N}$, the *substance* $\text{C}_{15}\text{H}_{23}\text{O}_8\text{N}$, which crystallised in colourless needles melting at 110° , was formed.

β -Dicyanoacetylacetone (*cyanoiminomethylacetylacetone*) is obtained by the action of acetic acid or very dilute hydrochloric acid on the α -compound, and crystallises in pale yellow needles melting at 227° . The corresponding γ -compound is obtained when the α -compound is treated with the molecular quantity of ethylaniline in alcoholic solution, and separates as insoluble plates melting at 211° . The δ -compound is yellowish-green, melts at 162° , and is scarcely soluble in sodium hydroxide. The α -compound is characterised by the fact that it is easily decomposed by alkali hydroxides into hydrocyanic acid and cyanoacetylacetone, and is alone able to combine with methylene compounds and bases. By sulphuric acid, the α compound is destroyed, whilst the isomerides form coloured solutions; the α -compound alone gives a coloration with ferric chloride.

Dicyanodiacylacetone (symmetrical *$\alpha\delta$ -tetra-acetyl- $\beta\gamma$ -di-iminobutane*) is most readily prepared by warming a mixture of acetylacetone, dicyanoacetylacetone, and sodium ethoxide in alcoholic solution. *Ethyl α -carboxy- $\beta\gamma$ -di-imino- $\delta\delta$ -diacetylvalerate*,



is prepared from mol. quantities of ethyl sodiomalonate, and dicyanoacetylacetone, and forms white prisms melting at 141 — 142° .

Action of Cyanogen on Ethyl Benzoylacetate [With FELIX HEINEMANN.]—*Ethyl dicyanobenzoylacetate* (*ethyl cyanoiminomethylbenzoylacetate*), $\text{CN}\cdot\text{C}(\text{:NH})\cdot\text{CHBz}\cdot\text{CO}_2\text{Et}$, is prepared by passing cyanogen into a cooled alcoholic solution of ethyl benzoylacetate and sodium ethoxide, and forms crystals melting at $142\cdot5^\circ$; when kept in

contact with aqueous sodium hydroxide, hydrocyanic acid, and ethyl cyanobenzoylacetate, $\text{CN}\cdot\text{CHBz}\cdot\text{CO}_2\text{Et}$, are formed; the latter melts at 37.5° . The dicyano-ester is very stable towards acids, but treatment with hot concentrated sulphuric acid converts it into an isomeride which crystallises in insoluble needles melting at 184° . The ester yields an *additive* product with ammonia, $\text{C}_{13}\text{H}_{15}\text{O}_3\text{N}_3$, which forms prismatic crystals melting at 176° , and an *aniline* derivative, $\text{C}_{19}\text{H}_{19}\text{O}_3\text{N}_3$, which crystallises in hexagonal leaflets melting at 155° . The *additive* product with hydrogen sulphide, $\text{C}_{13}\text{H}_{14}\text{O}_3\text{N}_2\text{S}$, forms prismatic, yellow crystals melting at 160° , which rapidly become greenish-yellow; the compounds with bases are probably amidines.

Hydroxylamine (2 mols.) and ethyl dicyanobenzoylacetate (1 mol.) react with the elimination of 1 mol. of H_2O , 1 mol. of the hydroxylamine combining directly with the cyano-group and the other reacting with the carbonyl group of the ester; the compound thus formed, $\text{C}_{18}\text{H}_{16}\text{O}_4\text{N}_4$, forms colourless crystals melting and decomposing at 155° .

The *phenylhydrazone* of ethyl dicyanobenzoylacetate, $\text{C}_{19}\text{H}_{18}\text{O}_2\text{N}_4$, is crystalline and melts at 163° ; the *acetyl* compound, $\text{C}_{15}\text{H}_{14}\text{O}_4\text{N}_2$, crystallises in colourless plates melting at 111° . *Ethyl dicyanodibenzoylacetate* (*ethyl $\beta\gamma$ -di-imino- α -dibenzoyladipate*), $\text{C}_{24}\text{H}_{24}\text{O}_6\text{N}_2$, prepared by treating ethyl dicyanobenzoylacetate with sodium ethoxide and ethyl benzoylacetate, crystallises in leaflets melting at 156.5° .

Action of Cyanogen on Ethyl Cyanoacetate and Benzoylacetone [With W. SANDER].—*Ethyl dicyanocyanoacetate* (*ethyl cyanoimino-methylcyanoacetate*), $\text{CN}\cdot\text{C}(\text{:NH})\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$, prepared by passing cyanogen into a cooled alcoholic solution of ethyl cyanoacetate and sodium ethoxide, crystallises in yellow needles melting and decomposing at 162° . When molecular quantities of this ester and ethyl sodioacetoacetate are brought together in alcoholic solution, the *lactam* of ethyl dicyanocyanoacetoacetoacetate, $\text{CO}_2\text{Et}\cdot\text{CHAc}\cdot\text{C}\begin{smallmatrix} \text{C}(\text{:NH})\cdot\text{CH}\cdot\text{CN} \\ \text{N} \text{---} \text{CO} \end{smallmatrix}$, is obtained as a yellow, crystalline substance, sintering at 149° and melting completely at 168° . A similar *lactam*, $\text{C}_{10}\text{H}_9\text{O}_3\text{N}_3$, is obtained from ethyl dicyanocyanoacetate and acetylacetone by dissolving the two constituents in an alcoholic solution of sodium ethoxide and adding a dilute solution of sulphuric acid; it crystallises in yellowish-green plates melting at 175° . *Dicyanobenzoylacetone* (*cyanimino-methylbenzoylacetone*), $\text{CN}\cdot\text{C}(\text{:NH})\cdot\text{CHAcBz}$, is prepared by passing cyanogen into a well-cooled solution of benzoylacetone and sodium ethoxide in alcohol; it crystallises in yellow prisms melting at 118° or 121° ; the hydrogen sulphide *additive* product, $\text{C}_{12}\text{H}_{12}\text{O}_2\text{N}_2\text{S}$, forms yellow needles melting and decomposing at 182° . K. J. P. O.

Condensation of Bromoacetyl Glycol [α -Bromoethyl Acetate] with the Esters of Acetoacetic and Acetonedicarboxylic Acids. ALBIN HALLER and F. MARCH (*Compt. rend.*, 1904, 139, 99—101. Compare Abstr., 1901, i, 538; 1903, i, 318, 714; this vol., i, 180).—*Methyl γ -acetoxy- α -acetylbutyrate*, $\text{OAc}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHAc}\cdot\text{CO}_2\text{Me}$,

prepared by heating a molecular mixture of the sodium derivative of methyl acetoacetate and α -bromoethyl acetate at $140-150^\circ$, is a liquid boiling at $150-153^\circ$ under 12 mm. pressure, and reacts with semicarbazide to form the 3-methyl-4-acetoxyethylpyrazone-1-carboxylamide, $\text{OAc}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH} \begin{smallmatrix} \text{CO}-\text{N}\cdot\text{CO}\cdot\text{NH}_2 \\ \text{CMe:N} \end{smallmatrix}$, which crystallises from alcohol

and melts at 163° . *Ethyl γ -acetoxy- α -acetylbutyrate*, similarly prepared to the methyl ester, boils at $147-150^\circ$ under 13 mm. pressure and yields with semicarbazide the same pyrazolone as the methyl derivative. *Methyl α -acetoxyethylacetonedicarboxylate* (methyl β -keto- γ -acetoxy- α -acetoxyethylbutyrate),



prepared by heating a mixture of α -bromoethyl acetate and the sodium derivative of methyl acetonedicarboxylate at 120° for 1 hour, is an oil boiling at $152-155^\circ$ under 20 mm. pressure.

Ethyl α -acetoxyethylacetonedicarboxylate, similarly prepared from ethyl acetonedicarboxylate, is an oil boiling at $162-165^\circ$ under 20 mm. pressure. *Methyl γ - ϵ -dihydroxy- β :(δ or ζ)-dicarbomethoxyphenylacetate*, $\text{CO}_2\text{Me}\cdot\text{CH}_2\cdot\text{C}_6\text{H}(\text{OH})_2(\text{CO}_2\text{Me})_2$, melting at $143-143.5^\circ$, is a secondary product in the preparation of methyl α -acetoxyethylidicarboxylate; and, similarly, ethyl γ - ϵ -dihydroxydicarbomethoxyphenylacetate (compare Cornelius and Pechmann, Abstr., 1886, 802) is formed in the preparation of the ethyl derivative. M. A. W.

Normal Presence of Formaldehyde in the Products of Combustion and Smoke. AUGUSTE TRILLAT (*Compt. rend.*, 1904, 138, 1613—1615).—Various combustible substances, coal, peat, different kinds of wood, paper, pure cellulose, cork, caoutchouc, various tissues, and tobacco, were burnt in glass tubes in a current of air carefully purified from traces of formaldehyde, the gaseous products condensed in suitable receivers, and tested for formaldehyde by the dimethylaniline test; in all cases, formaldehyde was found in quantities varying from 1/1000 of the weight of the substance burnt to 1/100,000, the maximum quantity being given by the combustion of wood and cellulose materials. Similar results were obtained by the combustion of hydrocarbons; in the case of the aromatic series, the quantity of formaldehyde formed increased with the complexity of the homologue, thus benzene gave 1/120,000 of its weight of formaldehyde; toluene, 1/80,000; and xylene, 1/40,000 (compare Abstr., 1903, i, 222). Further, the nature of the walls of the furnace plays an important part in determining the amount of formaldehyde formed during combustion; from 12 grams of benzene burnt in a tube containing broken porcelain 0.0007 gram of formaldehyde was obtained, whilst from the same weight of benzene burnt at the same temperature in a tube filled with copper turnings, 0.078 gram was obtained. These experiments show that the formaldehyde present in atmospheric air (compare Henriet, this vol., i, 289, 649) is derived from the products of combustion.

M. A. W.

Combined Sulphurous Acids. WILHELM KERP (*Chem. Centr.*, 1904, ii, 57—58; from *Arb. Kais. Ges.-A.*, 21, 180—225).—Dextrose

sodium hydrogen sulphite, $\text{C}_6\text{H}_{12}\text{O}_6\cdot\text{NaHSO}_3$, prepared by passing sulphur dioxide for a long time into a solution of dextrose and sodium carbonate in water and precipitating with alcohol, crystallises in matted needles and is readily soluble in water and rather soluble in methyl alcohol. The aqueous solution is acid to litmus, and is oxidised much more readily on exposure to air than the acetaldehyde compound; on evaporation, a syrup is left, which gradually crystallises.

The dissociation constants of the hydrolytic decomposition of the sodium hydrogen sulphite compounds of the following substances have been determined, and are given below :

| | <i>N</i> -Solution. | 1/10 <i>N</i> -Solution. | 1/30 <i>N</i> -Solution. |
|--------------------|-----------------------|--------------------------|--------------------------|
| Formaldehyde..... | 0.13×10^{-6} | 0.12×10^{-6} | 0.11×10^{-6} |
| Acetaldehyde | 2.84×10^{-6} | 2.26×10^{-6} | 2.06×10^{-6} |
| Benzaldehyde | — | 1.00×10^{-4} | 1.10×10^{-4} |
| Acetone | 4.57×10^{-3} | 4.3×10^{-3} | 3.8×10^{-3} |
| Dextrose | 311×10^{-3} | 220×10^{-3} | 124×10^{-3} |

Under similar conditions, the quantities of free sodium hydrogen sulphite present in aqueous solutions of the compounds of acetaldehyde, benzaldehyde, acetone, and dextrose are respectively about 5, 31, 155, and 500—1200 times as great as that contained in a solution of the formaldehyde compound.

Rost has found that the combined sulphurous acid in these compounds has no characteristic pharmacological effect, the action being entirely due to the free sulphite. The poisonous action of these compounds can thus be approximately estimated by titrating the aqueous solution with iodine. Experiments have also shown that under certain conditions the physiological action of sulphurous acid contained in musts or fruits in which it is present as the dextrose compound is different to that of the acid present in wine in the form of the acetaldehyde compound.

The hydrolytic decomposition of the dextrose compound has also been determined by means of the polaristobometer. The results show that whilst the normal and seminormal solutions give practically the same dissociation constant, a decinormal solution yields a very much lower value.

E. W. W.

Rare Earths. WILHELM BILTZ (*Annalen*, 1904, 331, 334—358).—The thorium, didymium, praseodymium, neodymium, samarium, cerium, and lanthanum derivatives of acetylacetone can be prepared in nearly quantitative yields by adding solutions of salts of the earths to a faintly alkaline solution of acetylacetone in ammonia, and precipitating by addition of the smallest possible quantity of ammonia (compare Urbain, *Abstr.*, 1897, i, 236; and Urbain and Budischorsky, 1897, ii, 318). These compounds could not be used as a means for separating or identifying the rare earths, since not only do they closely resemble one another in solubility, but they also very readily form additive products with ammonia or substituted ammonias. The melting points are as follows: *thorium acetylacetone*, 171° ; *didymium acetylacetone*, 151 — 152° (from alcohol), 146 — 147° (from water),

142—144° (from carbon tetrachloride); *praseodymium acetylacetonate*, 146°; *neodymium acetylacetonate*, 144—146°; *samarium acetylacetonate*, 146—147°; *cerium acetylacetonate* (with $3\text{H}_2\text{O}$), 145° (anhydrous), 131—132°; *lanthanum acetylacetonate*, 185° (from alcohol). In several cases, the melting points are neither constant nor sharp.

Cryoscopic determinations of the mol. weight in organic solvents show that these substances are generally dimolecular. Alcoholysis of the more feebly basic earths was observed; in the case of thorium, it could be quantitatively followed.

Aluminium acetylacetonate, which has been long known, differs from the compounds here described by not being able to form additive compounds with ammonia and having a simple mol. weight in carbon disulphide.

Owing to the stability and ease of purification of thorium acetylacetonate, an attempt was made to redetermine the atomic weight of thorium by its means, but it was found in practice that it is impossible to ignite thorium oxide over the blowpipe to a constant weight. Absorption of air or gas appears to take place.

K. J. P. O.

Metallic Derivatives of Acetylacetonate. WILHELM BILTZ and JOHN A. CLINCH (*Zeit. anorg. Chem.*, 1904, 40, 218—224).—*Zirconium acetylacetonate*, $\text{ZrR}_4 \cdot 10\text{H}_2\text{O}$ (where R represents the acetylacetonate residue, $\text{C}_5\text{H}_7\text{O}_2$), is best prepared by adding acetylacetonate gradually to an aqueous solution of zirconium nitrate, sufficient sodium carbonate being simultaneously added to keep the acetylacetonate in solution. The solution must be kept faintly acid. The salt separates in hexagonal crystals. The anhydrous salt separates from ethyl alcohol in needles, softens at 185°, and melts at 194—195°. *Uranium acetylacetonate*, UR_4 , prepared by reducing uranyl acetate by sodium hydrogen sulphite and then adding acetylacetonate, separates from ether in brown or olive-green leaflets and melts indefinitely at 176°. *Uranyl acetylacetonate*, $\text{UO}_2\text{R}_2 \cdot \text{H}_2\text{O}$, prepared by the action of acetylacetonate on solutions of uranyl salts, is orange-yellow.

Determinations of the molecular weight of zirconium acetylacetonate in carbon tetrachloride by the ebullioscopic method gave figures corresponding with ZrR_4 . This behaviour is exceptional, since other rare earth derivatives of acetylacetonate undergo polymerisation in organic solvents.

Thorium acetylacetonate aniline, $(\text{ThR}_4)_2 \cdot \text{NH}_2\text{Ph}$, can be crystallised from ether without undergoing decomposition.

Didymium acetylacetonate pyridine, $\text{DiR}_3 \cdot \text{C}_5\text{H}_5\text{N}$, melts at 144—145°. *Cobalt acetylacetonate ammonia*, $\text{CoR}_2 \cdot (\text{NH}_3)_2$, forms a brown, crystalline precipitate. *Nickel acetylacetonate ammonia*, $\text{NiR}_2 \cdot (\text{NH}_3)_2$, forms pale blue crystals. *Cobalt acetylacetonate pyridine*, $\text{CoR}_2 \cdot (\text{C}_5\text{H}_5\text{N})_2$, forms dark red crystals and melts at 150—152°. *Cobalt acetylacetonate aniline*, $\text{CoR}_2 \cdot (\text{NH}_2\text{Ph})_2$, forms brown, silky needles and melts at 108°. *Nickel acetylacetonate pyridine*, $\text{NiR}_2 \cdot (\text{C}_5\text{H}_5\text{N})_2$, forms blue crystals. *Nickel acetylacetonate aniline*, $\text{NiR}_2 \cdot (\text{NH}_2\text{Ph})_2$, forms pale blue needles.

A. McK.

Birotation of Dextrose. ROBERT BEHREND and PAUL ROTH (*Annalen*, 1904, 331, 359—382).—In order to ascertain the cause of the birotation of dextrose, the subject has been investigated anew.

In pyridine solution, the birotation is very marked; $[\alpha]_D$ is at first 138.88° ; after 3 hours at the temperature of the room, 127.87° ; and after 24 hours, 71.17° . This fact excludes all possibility of the hydrate theory, since it is extremely improbable that pyridine can form an additive product with dextrose. It seems more probable that dextrose may exist in various isomeric forms of different optical activity.

A relation has been shown to exist between the various penta-acetates and the dextroses of different optical activity. Only two penta-acetates appear to exist, the α -compound melting at 110 — 111° , and the β -penta-acetate melting at 130 — 131° . The γ -penta-acetate described by Tanret (*Abstr.*, 1895, i, 321, 490), melting at 86° , appears to be a mixture of the α - and β -varieties. They are represented as being stereoisomeric

in the sense of the formulæ:
$$\begin{array}{ccccccc} & & & & \text{O} & & \\ & & & & \parallel & & \\ \text{OAc} & \text{OAc} & \text{H} & & \text{OAc} & & \\ | & | & | & & | & & \\ \text{---C---} & \text{C---} & \text{C---} & \text{C---} & \text{C---} & \text{CH}_2\cdot\text{OAc} \\ | & | & \text{OAc} & | & | \\ \text{H} & \text{H} & & \text{H} & \text{H} \end{array}$$

and
$$\begin{array}{ccccccc} & & & & \text{O} & & \\ & & & & \parallel & & \\ \text{H} & \text{OAc} & \text{H} & & \text{OAc} & & \\ | & | & | & & | & & \\ \text{---C---} & \text{C---} & \text{C---} & \text{C---} & \text{C---} & \text{CH}_2\cdot\text{OAc} \\ | & \text{H} & \text{OAc} & | & | \\ \text{OAc} & & & \text{H} & \text{H} \end{array}$$

When dextrose (m. p. 146°), which, when dissolved in water or pyridine, shows the higher rotation, is digested in pyridine with acetic anhydride, an acetyl derivative is obtained (m. p. 103 — 107°), from which the α -compound can be easily isolated. Keeping at the ordinary temperature increases the yield, whilst heating causes a decrease.

The β -penta-acetate is obtained, although in small yield, from a solution of dextrose in pyridine, which has acquired the lowest rotation either by heating or by keeping at 0° for 24 hours. Long keeping after the acetylation increases the yield. When solid dextrose is treated with pyridine and acetic anhydride, the same crude product is obtained.

It would appear, therefore, that since the crystalline dextrose (m. p. 146°) and the solution of higher rotation yield the α -penta-acetate, the α -compound has the same constitution as the dextrose of higher rotation. This is best expressed by giving dextrose the oxidic constitution. The solution of lower and constant rotation, which yields mainly the β -penta-acetate, contains a mixture in equilibrium of the two stereoisomerides.

It is suggested that the two dextroses should be called the α - and β -dextroses; the α -compound then corresponds to Tanret's α -dextrose, whilst the β -glucose is Tanret's γ -compound. The β -dextrose of Tanret is probably a mixture of the α - and β -dextroses. That the solution of lower and constant rotation contains a mixture of the α - and β -compounds is supported by the fact that the yield of β -penta-acetate obtained from it is but small.

It is further pointed out that it is possible that the α -dextrose is the aldehydic form of the sugar, and that the solution of constant rotation

contains either a mixture of the stereoisomeric oxidic forms, possibly in equilibrium with a certain amount of the aldehyde, or possibly a mixture of the aldehyde with β -dextrose.

Quantitative experiments on the acetylation have shown that theoretical yields are never obtained. From the solution of higher rotation, 79 per cent. of acetyl derivative is isolated, and from the solution of lower rotation, 66 per cent. From the former, about 64 per cent. of pure α -penta-acetate can be isolated by recrystallisation, and from the latter about 28 per cent. of β -penta-acetate can be obtained. Especial experiments were made to ascertain the properties of mixtures of α - and β -penta-acetates and it was thus found that the material obtained by acetylating dextrose consisted entirely of these two substances.

It has been found that the two dextrose acetates can probably be separated by the action of nitric acid when the β -compound is alone nitrated (compare Koenigs and Knorr, Abstr., 1902, i, 135). The nitration was effected by adding phosphoric oxide to a cooled solution of the sugar in nitric acid of sp. gr. 1.52. K. J. P. O.

Inulin. ARTHUR L. DEAN (*Amer. Chem. J.*, 1904, 32, 69—84).—Inulin has been prepared from *Dahlia varia'ilis*, *Inula helenium*, *Helianthus tuberosus*, *Lappa minor*, and certain species of *Solidago*; the products showed no essential differences and may therefore be regarded as identical; in each case, the inulin was found to be accompanied by lævulins. A determination of the molecular weight of inulin by the cryoscopic method gave a value 2329, but the experiment was inconclusive; the inulin employed had $[\alpha]_D - 38.6^\circ$.

Inulin cannot be obtained with $[\alpha]_D$ much higher than -40° ; such preparations appear to be unstable, and their rotatory power decreases on solution and reprecipitation. It is suggested that inulin is not a single, well-defined compound, but a mixture of molecular complexes which exhibit only slight differences in their properties. The lævulins are more soluble than inulin, have a smaller rotatory power, and are probably composed of complexes of smaller magnitude. E. G.

Molecular Weight of Glycogen. MADAME Z. GATIN-GRUZEWSKA (*Compt. rend.*, 1904, 138, 1631—1634).—Using the Nernst-Beegg apparatus and a Beckmann thermometer capable of being read to the 1/1000th and estimated to the 1/10,000th of a degree, the author has re-determined the molecular weight of glycogen by the cryoscopic method. The glycogen was extracted from dog's liver, carefully purified, and dried over calcium chloride (compare this vol., i, 295). 3.850 grams of the substance in 200 c.c. of aqueous solution gave a freezing point of 0.0001° , which corresponds with a molecular weight of 716,100, or, applying the correction obtained from comparative experiments on sugar candy, the molecular weight of glycogen is over 140,000. The author therefore concludes (1) that the hitherto accepted value (1620) for the molecular weight of glycogen, due to Sabrieff (compare Abstr., 1890, 1215), is incorrect, and (2) either glycogen is very slightly

soluble in water and its molecular weight is infinitely great, or it is insoluble in water and its molecular weight has not been determined.

M. A. W.

Constitution of Ammonium. JOSEPH A. LE BEL (*J. Chim. Phys.*, 1904, ii, 340—346).—The author had previously obtained two crystalline forms of trimethylisobutylammonium platinichloride, but the forms are reversible and dependent on temperature, and hence chemical isomerism is not definitely established. He has therefore endeavoured to obtain other substituted ammonium salts which exist in two forms, and finds that methyltripropylammonium platinichloride, however prepared, at first yields birefringent crystals which, in 24 hours, change to regular octahedral crystals. The ethyltripropylammonium compound also forms two sets of crystals, but the stability of those first formed is less, the change occurring within a quarter of an hour. The author, however, considers both these to be cases of polymerisation and not of isomerism, and hence that the four radicles united to ammonium occupy the same position.

L. M. J.

Constitution of the So-called Dithiocyanic Acid and Perthiocyanic Acid. ARTHUR HANTZSCH and M. WOLVEKAMP (*Annalen*, 1904, 331, 265—297).—Since, under the action of concentrated hydrochloric acid, the esters of dithiocyanic acid yield mercaptans and ammonium chloride exclusively, no alkylamine being formed, the older formulæ, which represent the alkyl group as being linked to the nitrogen, cannot be correct. The formula $SM' \cdot C \begin{smallmatrix} \diagup N \\ \diagdown \end{smallmatrix} C \cdot SM'$ does

not appear to be correct for the salts, since, in addition to the decomposition of the esters just mentioned, the esters and salts of dithiocyanic acid are only able to combine with 1 mol. of water or hydrogen sulphide. It is more probable that a true cyano-group is present, thus $C(SM')_2 \cdot N \cdot CN$, this supposition being in accord with the reaction of the esters just mentioned. Moreover, this formula accounts for the fact that the alkali salts are able to combine with hydrogen sulphide to form thiocarbamidodithiocarbonates, $C(SM')_2 \cdot N \cdot CS \cdot NH_2$; finally, the synthesis of dithiocyanates from cyanamide and carbon disulphide in an alkaline alcoholic solution clearly shows that dithiocyanates are cyanoaminodithiocarbonates, $CS_2 + CN \cdot NH_2 + 2KOH = C_2N_2S_2K_2 + 2H_2O$.

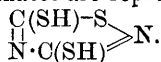
The free acid, which can be obtained from its salts in the form of yellow needles by treatment with hydrochloric acid at a low temperature, may have either the formula $C(SH)_2 \cdot N \cdot CN$ or $SH \cdot CS \cdot NH \cdot CN$; the latter is the more probable, since the acid, in spite of its low solubility, is not immediately precipitated by acids from its salts; further, the yellow colour points to a change of constitution.

The dimethyl ester, $C(SMe)_2 \cdot N \cdot CN$, prepared from methyl iodide and the potassium or silver salt, crystallises in colourless leaflets melting at 57° , and is converted by warming with concentrated hydrochloric acid into methyl carbamidodithiocarbonate, $C(SMe)_2 \cdot N \cdot CO \cdot NH_2$, which crystallises in white, stellate groups decomposing without melting at 217° . The formation of the same ester, in which both the alkyl groups

must be united to sulphur, from both the potassium and silver salts indicates that the salts are derivatives of an acid of the first type. The lead and silver salts decompose on heating into metallic sulphide and a yellow substance of low melting point, which is probably *cyanothiocarbimide*, $S:C:N\cdot CN$.

The cyanoamidocarbonates, prepared from cyanamide, carbon dioxide, and alcoholic potassium hydroxide, have probably the formula $(OM')_2C:N\cdot CN$, and not $(OM')\cdot CO\cdot NM\cdot CN$, as previously suggested.

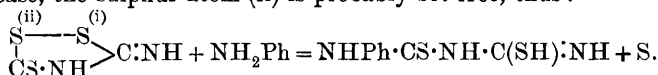
The fact that the alkyl perthiocyanates decompose into ammonia and mercaptan, no alkylamine being formed, points to the alkyl group being linked to sulphur. This fact was demonstrated in the case of the *dimethyl* ester, which is easily obtained pure in the form of crystals melting at 42° and boiling at 279° . The esters of perthiocyanic acid are more stable than those of cyanoamidodithiocarbonic acid, and do not form additive compounds with water. Similarly, the perthiocyanates are more stable than the cyanoamidodithiocarbonates; they neither form additive compounds with hydrogen sulphide nor decompose with the formation of metallic sulphides. These facts indicate that the perthiocyanates are represented by a ring formula,



The solid acid obtained from the perthiocyanates, xanthanic acid, does not possess the same constitution as the salts, but is probably re-

presented by the formula $\begin{array}{c} (ii) \quad (i) \\ S \text{---} S \\ | \quad | \\ CS\cdot NH \end{array} \gg C:NH$. Only such rings contain-

ing two atoms of sulphur in which the two atoms of sulphur are directly linked are decomposed by alkalis with the separation of sulphur; xanthanic acid is decomposed by potassium hydroxide into potassium cyanoaminodithiocarbonate and sulphur, the sulphur atom (i) in the above formula being most probably set free. Xanthanic acid and aniline readily react, giving phenyldithiobiuret and sulphur; in this case, the sulphur atom (ii) is probably set free, thus:



The other possible formula for xanthanic acid, $\begin{array}{c} S \text{---} S \\ | \quad | \\ C(SH):N \end{array} \gg C:NH$, is not in accord with the indifferent character of the substance.

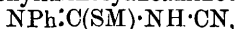
The transformation of xanthanic acid into salts of perthiocyanic acid through the intermediate stage of cyanoaminodithiocarbonate, which combines with the sulphur set free by the alkali, can be followed in certain cases.

The *acetyl* derivative of xanthanic acid, $\begin{array}{c} S \text{---} S \\ | \quad | \\ CS\cdot NH \end{array} \gg C:NAc$, prepared by direct acetylation, undergoes, under the influence of alkalis, the same decomposition as xanthanic acid.

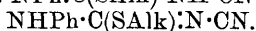
The constitution of xanthanic acid above demonstrated shows that it may be called *5-thio-2-imino-3:4-disulphoazolidine*.

Thiuret (Fromm, Abstr., 1893, i, 575) is shown to be a sulphoazo-

lidine derivative, since it can be obtained by oxidising phenyldithiobiuret and is reconverted into that substance by reduction, and is decomposed by alkali hydroxides in the same way as xanthanic acid, sulphur and a salt of phenyliminocyanaminothiocarbonate,



being formed. The esters obtained from the salts of the acid last mentioned are identical with those obtained from the product of condensation of phenylthiocarbimide and sodium cyanoamide. The alkyl group must be attached to the sulphur atom and the compound have either the formula $\text{NPh}\cdot\text{C}(\text{SAlk})\cdot\text{NH}\cdot\text{CN}$ or



The salts of phenyliminocyanaminothiocarbonic acid are not able to recombine with sulphur as are those of cyanoamidodithiocarbonic acid.

The so-called oxides and sulphides of the thiocarbimides (Freund, Abstr., 1895, i, 576) probably both have five-membered rings; thus the oxides have the formula $\begin{array}{c} \text{S} \text{---} \text{S} \\ | \quad \diagup \\ \text{CO}\cdot\text{NR} \end{array} > \text{C}\cdot\text{NR}$, and the sulphides the

formula $\begin{array}{c} \text{S} \text{---} \text{S} \\ | \quad \diagup \\ \text{CS}\cdot\text{NR} \end{array} > \text{C}\cdot\text{NR}$. On reduction, they behave as does xanthanic acid, yielding dialkylthiocarbamides. The oxides react with aniline, phenylthiobiuret and sulphur being formed.

The sulphides, which are feebly basic, do not react with aniline, because it is not possible for them to assume the tautomeric form with the group $\text{N}\cdot\text{CSH}$, as is the case with xanthanic acid, or it is possible that they pass on heating into a more stable form (as was observed by Freund in the case of the dimethyl ester) which no longer contains the disulphoazole ring, but is a diazosulphole derivative.

These sulphides may, however, have the formula $\begin{array}{c} \text{S} \text{---} \text{NR} \\ | \quad \diagup \\ \text{CS}\cdot\text{NR} \end{array} > \text{CS}$.

The diazosulpholidine and the disulphoazolidine compounds may be distinguished by their different behaviour towards reducing agents, aniline, and alkalis. The latter yield with reducing agents thiocarbamides, with aniline, sulphur is eliminated, and with alkali, sulphur is set free and cyanoamido-derivatives are formed. The former, on the other hand, react with aniline, are not reduced to thiocarbamides, and do not lose sulphur under the influence of alkalis.

K. J. P. O.

Solubilities and Polymerisation of Cyanogen. MARCELLIN BERTHELOT (*Compt. rend.*, 1904, 138, 1649—1652).—The author has examined the behaviour of cyanogen towards various solvents with the following results. (1) Water at 20° absorbs the gas slowly, but indefinitely; decomposition of the solution occurs at the same time with liberation of carbon dioxide. (2) Absolute alcohol at 20° absorbs cyanogen rapidly, but indefinitely, a brown precipitate is formed, and the liquid has a strong odour recalling that of carbylamine; by the action of water, two substances, one soluble and the other insoluble, are separated from the final product; the results of analyses of these two substances show that they are formed by polymerisation of the cyanogen and its condensation with alcohol. (3) Glacial acetic acid

absorbs 42 vols. of the gas per unit volume of liquid, the quantity rising to 50.5 vols. after 3 days; the solution contains free cyanogen, and, in addition, a small proportion of a polymerised product. (4) Chloroform absorbs 19 vols. of the gas per unit volume, the quantity rising to 29—30 vols. after some time; the solution contains free cyanogen. (5) and (6) Benzene and turpentine form solutions of cyanogen, containing respectively 28 and 9—10 vols. per unit volume.

M. A. W.

The Behaviour of Cyanogen towards Potassium Cyanide. MARCELLIN BERTHELOT (*Compt. rend.*, 1904, 138, 1653—1657).—Aqueous solutions of potassium cyanide absorb indefinite quantities of cyanogen, the potassium cyanide undergoes decomposition, the cyanogen is polymerised and carbon dioxide evolved; two substances were isolated from the final product, one insoluble, corresponding with the molecular compound $3\text{CN}, 2\text{H}_2\text{O}$, and the other soluble, containing potassium. A solution of potassium ferrocyanide, or of potassium cyanide, in dilute acetic acid or alcohol also absorbs cyanogen with the formation of polymerised and condensation products.

M. A. W.

Thermochemical Studies on the Solution and Polymerisation of Cyanogen. MARCELLIN BERTHELOT (*Compt. rend.*, 1904, 139, 93—97. Compare preceding abstracts).—The heat developed by the solution of cyanogen in water is about 8.77 Cal. for each molecule of cyanogen, but owing to the polymerisation and chemical reaction which occur, the solution continues to develop heat slowly and at a decreasing rate, for some hours. The addition of a solution of potassium cyanide to an aqueous solution of cyanogen is accompanied by a heat development of 21.6 Cal. for each molecule of cyanogen. This is due to the polymerisation, condensation, and hydration induced by the action of the salt on the cyanogen. Alcohol dissolves cyanogen with a development of 9.28 Cals. for each molecule of cyanogen, and the addition of an alcoholic solution of potassium cyanide causes a further development of 5 Cals. for each molecule of cyanogen, or 81.2 Cals. for the ratio $\text{KCN} + 16\text{CN}_2$.

M. A. W.

Hydroxamic Acids. LUIGI FRANCESCONI and A. BASTIANINI (*Gazzetta*, 1904, 34, i, 428—434).—The amides of the monobasic acids with low molecular weight, such as acetamide, propionamide, and butyramide, react readily with hydroxylamine hydrochloride at the ordinary temperature yielding the corresponding hydroxamic acids. Capronamide reacts with hydroxylamine hydrochloride only at 100°, but, if moistened with alcohol, at the ordinary temperature. Chloroacetamide, on heating, yields the corresponding chloroacetohydroxamic acid. Among the aromatic amides, benzamide does not react with hydroxylamine hydrochloride, even at 100°. Carbamide, oxamide, succindiamide, and phthaldiamide only react above 100°, at which temperature the products formed decompose.

Chloroacetohydroxamic acid, $\text{CH}_2\text{Cl}\cdot\text{C}(\text{OH})\text{:N}\cdot\text{OH}$, crystallises from benzene in nacreous laminae which melt and decompose at 108° and

dissolve in alcohol, water, or ether; it has a faintly acid reaction, colours ferric chloride solution an intense red, gives a voluminous green precipitate with copper acetate, and reduces Fehling's solution.

Butyrohdroxamic acid melts at 127°, is extremely soluble in alcohol or water, and gives an intensely red coloration with ferric chloride.

T. H. P.

Azines of Ethyl β -Ketocarboxylates. LUDWIG WOLFF (*Ber.*, 1904, 37, 2827—2836. Compare *Abstr.*, 1903, i, 203; Betti, *Abstr.*, 1903, i, 78; this vol., i, 533).—*Ethyl azoacetoacetate*,



is obtained as an oil on the addition of hydrazine sulphate and sodium carbonate to ethyl acetoacetate in aqueous solution. It crystallises from dilute alcohol in colourless needles, melts at 47—48°, is easily soluble in ether, chloroform, or benzene, and gives a colour reaction with ferric chloride only after some time. It reacts with hydrazine in alcoholic solution to form 3-methylpyrazolone; when acted on by hydrochloric acid, it yields ethyl acetoacetate, 3-methylpyrazolone, and 5-ethoxy-3-methylpyrazole; with nitrous acid, it yields ethyl azo-isonitrosoacetoacetate.

Methyl azoacetoacetate is an oil at -20°, gives a red coloration with alcoholic ferric chloride after some minutes, and is decomposed by cold aqueous sodium hydroxide or when heated to 170—200°, with formation of crystalline products. When acted on by cold dilute hydrochloric acid, it yields methyl acetoacetate, 3:4-dimethylpyrazolone, and 5-ethoxy-3:4-dimethylpyrazole.

Contrary to Betti's statement, the substance formed by the action of hydrazine on ethyl isonitrosoacetoacetate is ethyl azoisonitrosoacetoacetate, $\text{N}_2\text{[CMe}\cdot\text{C(NO)}\cdot\text{CO}_2\text{Et}]_2$, and not ethyl bisdiazocetoacetate (*loc. cit.*). It crystallises in yellow plates, melts at 194°, and is converted slowly by cold mineral acids, quickly by warm alcoholic hydrochloric acid, into 4-isonitroso-3-methylpyrazolone, which melts at 232°.

5-Ethoxy-3:4-dimethylpyrazole, formed by heating methyl acetoacetate with hydrazine sulphate in aqueous solution, crystallises in matted, colourless needles, melts at 93°, and forms the *nitroso*-compound, $\text{N}\begin{smallmatrix} \text{CMe} & \text{---} & \text{CMe} \\ \diagdown & & \diagup \\ \text{N(NO)} & \cdot & \text{C} \end{smallmatrix}\begin{smallmatrix} \text{OEt} \\ | \\ \text{OEt} \end{smallmatrix}$, which is obtained as a yellow, crystalline mass and melts at 34°.

3:4-Dimethylpyrazolone crystallises in colourless prisms and melts at 268°.

5-Ethoxy-3-methylpyrazole is formed along with 3-methylpyrazole when ethyl acetoacetate is heated with hydrazine sulphate in aqueous solution. It crystallises in glistening, white needles, melts at 66—67°, and is hydrolysed by sulphuric acid at 146—150° to 3-methylpyrazolone. The solution of the hydrochloride gives an oily precipitation with gold chloride and a crystalline precipitate with mercuric chloride. The *nitroso*-compound, $\text{N}\begin{smallmatrix} \text{CMe} & \text{---} & \text{CH} \\ \diagdown & & \diagup \\ \text{N(NO)} & \cdot & \text{C} \end{smallmatrix}\begin{smallmatrix} \text{OEt} \\ | \\ \text{OEt} \end{smallmatrix}$, is a yellow oil which solidifies to yellow crystals and melts at 40°, and is converted by warm water

or alcohol into the isomeric substance $N \leq \begin{matrix} \text{CMe}-\text{C}\cdot\text{NO} \\ \text{NH}-\text{C}\cdot\text{OEt} \end{matrix}$. This is obtained in an unstable, green, crystalline modification which melts and decomposes at about 100° and changes, spontaneously or when dissolved in cold sodium hydroxide solution and reprecipitated by cold hydrochloric acid, into a stable modification which crystallises in delicate needles, melts and decomposes at $126-127^\circ$, is soluble in aqueous sodium carbonate, and yields isonitrosomethylpyrazolone (m. p. 232°) when treated with cold dilute hydrochloric acid. G. Y.

Semicarbazones of isoNitrosoketones and of Acyldinitrohydrocarbons. GIACOMO PONZIO (*Gazzetta*, 1904, 34, i, 410—414).—isoNitrosodiethyl-ketone-semicarbazone, $\text{NOH}\cdot\text{CMe}\cdot\text{Cet}\cdot\text{N}_2\text{H}\cdot\text{CO}\cdot\text{NH}_2$, crystallises from alcohol in white prisms melting and decomposing at 219° and is slightly soluble in acetic acid or water.

isoNitrosomethyl-propyl-ketone-semicarbazone,
 $\text{NOH}\cdot\text{Cet}\cdot\text{CMe}\cdot\text{N}_2\text{H}\cdot\text{CO}\cdot\text{NH}_2$,
 crystallises from alcohol in long, white needles melting and decomposing at 222° and dissolves to a slight extent in acetic acid or water.

isoNitrosoethyl-isobutyl-ketone-semicarbazone,
 $\text{NOH}\cdot\text{CMe}\cdot\text{C}(\text{CH}_2\cdot\text{CHMe}_2)\cdot\text{N}_2\text{H}\cdot\text{CO}\cdot\text{NH}_2$,
 crystallises from alcohol in white prisms melting and decomposing at 203° and is slightly soluble in water or acetic acid.

Propionyldinitroethane-semicarbazone,
 $\text{CMe}(\text{NO}_2)_2\cdot\text{Cet}\cdot\text{N}_2\text{H}\cdot\text{CO}\cdot\text{NH}_2$,
 crystallises from chloroform in white prisms melting and decomposing at $147-148^\circ$ and is soluble in alcohol, ether, or benzene.

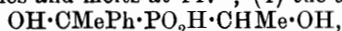
Acetyldinitropropane-semicarbazone, $\text{Cet}(\text{NO}_2)_2\cdot\text{CMe}\cdot\text{N}_2\text{H}\cdot\text{CO}\cdot\text{NH}_2$, separates from chloroform in white plates melting and decomposing at $143-144^\circ$ and dissolves in benzene, water, alcohol, or ether. It is remarkable that, whilst the action of nitrogen peroxide on isonitrosomethyl-propyl-ketone results in the replacement of the NOH group by N_2O_3 , yielding amylketopseudonitrole, the action of nitrogen peroxide on the semicarbazone of this ketone transforms the NOH group into N_2O_4 .

isoValeryldinitroethane-semicarbazone,
 $\text{CMe}(\text{NO}_2)_2\cdot\text{C}(\text{CH}_2\cdot\text{CHMe}_2)\cdot\text{N}_2\text{H}\cdot\text{CO}\cdot\text{NH}_2$,
 crystallises from chloroform in white prisms melting and decomposing at $148-149^\circ$ and is soluble in alcohol, ether, or benzene. T. H. P.

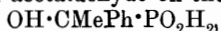
Some Mixed Derivatives of Hypophosphorous Acid. CHARLES MARIE (*Compt. rend.*, 1904, 138, 1707—1709. Compare Abstr., 1901, i, 635; 1902, i, 71, 255; 1903, i, 328, 379, 678).—The author has prepared the following acids either by the action of an aldehyde on a monoketone derivative of hypophosphorous acid, $\text{CH}\cdot\text{CRR}^1\cdot\text{PO}_2\text{H}_2$, or by the action of a ketone or another aldehyde on a monoaldehydic derivative of hypophosphorous acid, $\text{OH}\cdot\text{RCH}\cdot\text{PO}_2\text{H}_2$; (1) the acid $\text{OH}\cdot\text{CMe}_2\cdot\text{PO}_2\text{H}\cdot\text{CHPh}\cdot\text{OH}$, obtained by the action of benzaldehyde on the acid, $\text{OH}\cdot\text{CMe}_2\cdot\text{PO}_2\text{H}_2$, melts at 182° , is soluble in water, alcohol, or acetone, and insoluble in chloroform or benzene; (2) the acid

$\text{OH}\cdot\text{CMe}_2\cdot\text{PO}_2\text{H}\cdot\text{CH}(\text{C}_6\text{H}_{13})\cdot\text{OH}$,
 obtained by the action of heptaldehyde on the acid $\text{OH}\cdot\text{CMe}_2\cdot\text{PO}_2\text{H}_2$,

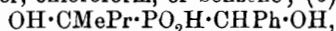
crystallises in brilliant spangles melting at 131° , is soluble in alcohol or acetone, and almost insoluble in cold water or ether; (3) the *acid* $\text{OH}\cdot\text{CMeEt}\cdot\text{PO}_2\text{H}\cdot\text{CH}(\text{C}_6\text{H}_{13})\cdot\text{OH}$, similarly prepared to the preceding, has similar properties and melts at 147° ; (4) the *acid*



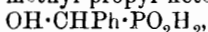
obtained by the action of acetaldehyde on the acid



melts at 192° , is very soluble in methyl or ethyl alcohol, very slightly so in acetone, and almost insoluble in benzene or chloroform; (5) the *acid*, $\text{OH}\cdot\text{CET}_2\cdot\text{PO}_2\text{H}\cdot\text{CHPh}\cdot\text{OH}$, obtained by the action of acetaldehyde on the acid, $\text{OH}\cdot\text{CET}_2\cdot\text{PO}_2\text{H}_2$, melts at 192° , is very slightly soluble in warm water or acetone, soluble in methyl or ethyl alcohol, and insoluble in ether, chloroform, or benzene; (6) the *acid*

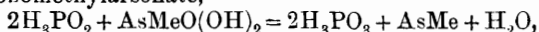


obtained by the action of methyl propyl ketone on the acid



melts at 170° , is soluble in methyl or ethyl alcohol, and insoluble in ether, benzene, or chloroform; (7) the *acid* $\text{OH}\cdot\text{CMe}_2\cdot\text{PO}_2\text{H}\cdot\text{CHMe}\cdot\text{OH}$, obtained by the action of acetaldehyde on the acid $\text{OH}\cdot\text{CMe}_2\cdot\text{PO}_2\text{H}_2$, melts at 132° and has the same solubility as the preceding compound; (8) the *acid* $\text{OH}\cdot\text{CH}_2\cdot\text{PO}_2\text{H}\cdot\text{CHPh}\cdot\text{OH}$, obtained by the action of benzaldehyde on the *acid* $\text{OH}\cdot\text{CH}_2\cdot\text{PO}_2\text{H}_2$, melts at 154° , is soluble in water, methyl or ethyl alcohol, and insoluble in ether, benzene, or chloroform; (9) the *acid* $\text{OH}\cdot\text{CHPh}\cdot\text{PO}_2\text{H}\cdot\text{CH}(\text{C}_4\text{H}_9)\cdot\text{OH}$, obtained by the action of isovaleric aldehyde on the acid $\text{OH}\cdot\text{CHPh}\cdot\text{PO}_2\text{H}_2$, melts at $203-205^{\circ}$, is soluble in boiling water, ethyl or methyl alcohol, or acetone, and slightly soluble in cold water or ether. M. A. W.

Methylarsine. VICTOR AUGER (*Compt. rend.*, 1904, 138, 1705—1707. Compare this vol., i, 22).—*Methylarsine*, $(\text{CH}_3\text{As})_4$, obtained by the action of sodium hypophosphite and sulphuric acid on sodium monomethylarsonate,



is a pale yellow oil, boiling at 190° under 15 mm. pressure, has a high specific gravity, and a strong garlic odour; it does not mix with water, is slightly soluble in alcohol, dissolves in hot acetic acid, and is very soluble in benzene; is not attacked by alkali hydroxides; is oxidised to methylarsenoxide by hot strong sulphuric acid, or by exposure to the air, or very rapidly in benzene solution; nitric acid oxidises it to methylarsonic acid, the halogens form corresponding derivatives, AsMeX_2 , and the alkyl iodides react more or less readily according to the equation $2\text{AsMe} + 3\text{MeI} = \text{AsMeI}_2 + \text{AsMe}_4\text{I}$. Methylarsine is readily polymerised by hydrochloric acid to a brownish-black powder resembling arsenic, insoluble in the ordinary solvents, readily oxidised by nitric acid to methylarsonic acid; at 160° it behaves like the liquid polymeride towards methyl iodide, and is quantitatively converted into arsenic and trimethylarsine by dry distillation in an atmosphere of hydrogen, $3\text{AsMe} = \text{AsMe}_3 + \text{As}_2$. The brown compound obtained by Bougault (*Abstr.*, 1903, ii, 339) by reducing methylarsonic acid by hypophosphorus acid in the presence of hydrochloric acid was probably this polymeride of methylarsine, and not arsenic, as described.

Ethylarsine is a yellow oil which does not polymerise so readily as methylarsine. M. A. W.

[Cacodylic Acid. Reply to von Zawidzki.] ARTHUR HANTZSCH (*Ber.*, 1904, 37, 2705—2708. Compare this vol., i, 381; and von Zawidzki, *Abstr.*, 1903, i, 801; this vol., i, 564).—Largely polemical. It is pointed out that the concentration of hydroxyl ions in solutions of the acid must be less than in the case of water, and not greater, as stated by Zawidzki. The reaction with hydrochloric acid is most readily explained by supposing that a chloride is formed, and, as this is only slightly ionised, it is relatively stable. J. J. S.

Freezing Point of Nitrobenzene. FR. C. C. HANSEN (*Zeit. physikal. Chem.*, 1904, 48, 593—595).—The freezing point of pure nitrobenzene is generally given as 5.3°, but it appears that such samples contain a trace of moisture, for after desiccation over concentrated sulphuric acid, or vigorous boiling for a few minutes and removal of the vapour, the freezing point rises to 5.7°. Benzene is similarly, although to a less extent, sensitive to traces of moisture. J. C. P.

Symmetric Diphenyl Derivatives. FRITZ ULLMANN [with EMILIO GILLI, OSCAR LOEWENTHAL, and GUSTAV M. MEYER] (*Annalen*, 1904, 332, 38—81).—Diphenyl and substituted diphenyls can be most readily prepared by heating iodobenzene or substituted iodobenzenes with copper at a temperature of 210—220°; in the case of substances boiling below 220°, the material is enclosed in a sealed tube, whilst with substances of higher boiling point open vessels may be used. The copper was the "naturkupfer C" of the firm of Bernh. Ullmann & Co., of Fürth; the use of other metals, such as magnesium, zinc, iron, or silver, is not to be recommended. This method of preparing diphenyls is far superior to Fittig's method, as the yield is nearly quantitative, and the material free from impurity.

I. *Hydrocarbons*.—When equal weights of iodobenzene and copper are heated for three hours in a sealed tube at 230°, the product extracted with ether, and the residue from the ether recrystallised from alcohol, pure diphenyl in a yield of 82 per cent. is obtained. By Fittig's method, only 5 per cent. is obtained. 2:2'-Dimethyldiphenyl is prepared from *o*-iodotoluene (b. p. 207° under 726 mm. pressure; Kekulé records 211°, and Edinger and Goldberg 202°) and copper in the same manner, and purified by fractionation; it forms large crystals melting at 17.8° and boiling at 258° under 737.6 mm. pressure; Fittig gives the boiling point as 272°, Zincke and Luginin as 277—282°, and Jacobson as 245—260°. The yield amounted to 63 per cent. 3:3'-Dimethyldiphenyl is prepared by heating *m*-iodotoluene (b. p. 211° under 734 mm. pressure; according to Beilstein and Kuhlberg, it boils at 204°) with copper at 240°; it is a colourless oil boiling at 283° under 718 mm. pressure. 4:4'-Dimethyldiphenyl is obtained in a yield of 54 per cent. by adding copper slowly to molten *p*-iodotoluene (b. p. 213.5° under 733 mm. pressure)

at 210°, and then raising the temperature to 260°; the crystalline product is extracted with alcohol, when the diphenyl is obtained as leaflets melting at 122°, and boiling at 295° under 760 mm. pressure (compare Zincke and Weiler).

The dixilyls, prepared by Fittig (*Annalen*, 1868, 147, 38), Oliveri (*Gazzetta*, 1882, 12, 158), and O. Jacobson (*Ber.*, 1881, 14, 2112), were not pure. 2:2':4:4'-*Tetramethyldiphenyl* was prepared by adding copper to 4-iodo-1:3-dimethylbenzene (b. p. 230° under 742 mm. pressure) heated to 228—230°, and then raising the temperature to 260°; the hydrocarbon forms orthorhombic crystals [$a:b:c=0.64075:1.0:50192$] melting at 41° and boiling at 288° under 722 mm. pressure. 2-Iodo-1:4-dimethylbenzene, $C_8H_8IME_2$, prepared by adding potassium iodide to diazotised *p*-xylydine, is a colourless liquid boiling at 230° under 722 mm. pressure (Edinger and Goldberg give the boiling point as 217°), and has a sp. gr. 1.5988 at 17°. 2:2':5:5'-*Tetramethylbenzene*, prepared from the iodo-derivative just described, forms colourless crystals melting at 50° and boiling at 284° under 732 mm. pressure.

2:2':4:4':5:5'-*Hexamethyldiphenyl* is prepared from 5-iodo-1:2:4-trimethylbenzene, which is obtained from ψ -cumidine and forms crystals melting at 52° and boiling at 320° under 738 mm. pressure. 2:2':4:4':6:6'-*Hexamethyldiphenyl* could not be obtained by Jannasch and Weiler (*Abstr.*, 1895, i, 604, and 1900, i, 213) by Fittig's method, but it was prepared although in somewhat small yield, by heating iodomesitylene with copper at 260—270°; it forms colourless, transparent, monoclinic crystals [$a:b:c=1.2892:1.?:\beta=95^\circ48'$] melting at 100.5° and boiling at 296° under 735 mm. pressure.

2:2'-Dinaphthyl (m. p. 287°) was prepared from 2-iodonaphthalene in a yield of 67.5 per cent. by heating with copper. 4:4'-Diphenyldiphenyl was prepared from 4-iododiphenyl (prepared from 4-nitrodiphenyl, and forming crystals melting at 111°) by heating at 250—270° with copper and then extracting the product with benzene, when a yield of 82.5 per cent. was obtained (Noyes and Ellis, *Abstr.*, 1896, i, 51, obtained a yield of 5 per cent. when sodium and *p*-bromodiphenyl were used); it forms lustrous leaflets melting at 320°, and does not give the coloration with sulphuric acid which the natural hydrocarbon, "benzerythrene," is observed to show—a coloration which must therefore be due to an impurity.

II. *Halogen Derivatives*.—When chloriodobenzenes are heated with copper, only the iodine is eliminated, good yields of chlorodiphenyls being obtained. 3:3'-*Dichlorodiphenyl*, thus prepared, forms colourless, transparent crystals melting at 23° and boiling at 322—324°; the yield was 67 per cent. 4:4'-*Dichlorodiphenyl* was obtained in a yield of 82 per cent. from *p*-chloriodobenzene, and melted at 148° and boiled at 315° (compare *Jahresbericht*, 1866, 463). 2:2':4:4'-*Tetrachlorodiphenyl* was prepared from 1:3-dichloro-4-iodobenzene (obtained in the ordinary way from 2:4-dichloroaniline) and formed crystals melting at 83° and boiling at 350—360°. 2:2':4:4':6:6'-*Hexachlorodiphenyl*, prepared from 1:3:5-trichloro-2-iodobenzene (m. p. 55° and b. p. 297° under 735 mm. pressure), forms quadratic crystals melting at 112.5°.

Bromiodobenzenes are only converted into diphenyls by heating with copper in a very imperfect manner; 3:3'-dibromophenyl (m. p. 53°) was obtained in very small yield from *m*-bromiodobenzene.

III. *Sulphonic Acid Derivatives*.—Neither the calcium salt, the amide, nor the anilide of *p*-iodobenzenesulphonic acid reacts with copper to form diphenyls, but *p*-iodobenzenesulphonmethylanilide, a compound in which no hydrogen remains attached to the nitrogen, does so react. *p*-Iodobenzenesulphonic anilide, $C_6H_4I \cdot SO_2 \cdot NHPh$, prepared from the sulphonic chloride, crystallises in leaflets melting at 143° and is readily methylated by the use of dimethyl sulphate; *p*-iodobenzenesulphonmethylanilide, $C_6H_4I \cdot SO_2 \cdot NMePh$, crystallises in leaflets melting at 111°, and, when heated with copper at 210–240°, is converted into 4:4'-diphenyldisulphondimethylanilide, which forms grey leaflets melting at 187°.

IV. *Nitro-derivatives*.—The conversion of halogen nitrobenzenes into nitrodiphenyls has been previously described (Abstr., 1901, i, 586).

V. *Amino-derivatives*.—Only when the hydrogen atoms of the amino-group are replaced by an alkyl and a sulphonic group was it found possible to obtain amino-derivatives of diphenyl. *m*- and *p*-Iodoaniline, *p*-iodoacetanilide, and *p*-iododimethylaniline give negative results when heated with copper. *p*-Toluenesulphon-*m*-iodoanilide, $C_7H_7 \cdot SO_2 \cdot NH \cdot C_6H_4I$, was prepared from *m*-iodoaniline and *p*-toluenesulphonic chloride, and forms colourless crystals melting at 128°; by means of dimethyl sulphate, it was converted into *p*-toluenesulphon-*m*-iodomethylanilide, $C_7H_7 \cdot SO_2 \cdot NMe \cdot C_6H_4I$, which crystallises in colourless needles melting at 81°. *Di-p*-toluenesulphon-3:3'-methylamino-diphenyl, prepared from the preceding compound, forms white, lustrous crystals.

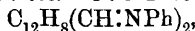
VI. *Phenol Derivatives*.—Although the iodophenols do not react readily with copper, the alkyl derivatives of the phenols give excellent yields of diphenyls. 2:2'-Dimethoxydiphenyl is obtained in a yield of 88 per cent. from *o*-iodoanisole (compare Jannasch and Köllitz, Abstr., 1898, i, 190; Diels and Bibergeil, Abstr., 1902, i, 219); it melts at 154° and gives, when heated with alcohol and fuming hydrochloric acid, diphenylene oxide. The *p*-toluenesulphonic ester of *o*-iodophenol, $C_6H_4I \cdot O \cdot SO_2 \cdot C_7H_7$, was prepared from the *p*-toluenesulphonic ester of *o*-nitrophenol, which was reduced to the amino-compound, the latter diazotised, and then treated with potassium iodide; it forms yellow plates melting at 73°. When heated with copper at 260° and the product extracted with alcohol, the *p*-toluenesulphonic ester of 2:2'-dihydroxydiphenyl was obtained; it crystallises in colourless needles melting at 171°.

The benzoates of 3:3'-dihydroxydiphenyl have also been prepared by a similar method, but only small yields were obtained. The *m*-iodophenol was, after other attempts, prepared by Noeltling and Stricker's method (Abstr., 1888, 262) from *m*-iodoaniline; the benzoate, prepared by the Schotten-Baumann process, forms slightly coloured crystals melting at 70°; when heated with copper at 215–260°, a small amount of the benzoate of 3:3'-dihydroxydiphenyl was obtained by extracting the product of the reaction with benzene; it forms white needles melting at 92°.

4 : 4'-Dimethoxydiphenyl was obtained in a yield of 85 per cent. from *p*-iodoanisole and copper, and melted at 173° (compare Gillmeister, Abstr., 1898, i, 138). 4 : 4'-Diethoxydiphenyl was obtained in a similar manner from *p*-iodophenetole, and melted at 176° (compare Hirsch, Abstr., 1889, 510). In order to prepare 2 : 2' : 5 : 5'-tetramethoxydiphenyl, 2-iodo-1 : 4-dimethoxybenzene was obtained by the usual methods from nitro-1 : 4-dimethoxybenzene as a yellow liquid boiling at 285° under 728 mm. pressure; the diphenyl, prepared in the usual manner with a yield of 93 per cent., formed pale yellow crystals melting at 104°, and, when boiled with 50 per cent hydrobromic acid and stannous chloride, was converted into a tetrahydroxydiphenyl (diquinol; m. p. 237°), previously obtained by Barth and Schreder (Abstr., 1885, 520).

VII. *Carboxylic Acid Derivatives*.—Methyl 2 : 2'-diphenyldicarboxylate is very readily obtained in a yield of 82 per cent. by heating methyl *o*-iodobenzoate with copper at 200–260°, extracting the product with ether, and fractionating the residue; the substance melted at 74.5° (compare Schultz, *Annalen*, 1880, 203, 98). Methyl *m*-iodobenzoate, prepared from *m*-iodobenzoic acid, crystallised in colourless needles melting at 50° and boiling at 276–277° under 739 mm. pressure, and was converted into methyl 3 : 3'-diphenyldicarboxylate by heating with copper at 260° and extracting the product with methyl alcohol; it melts at 104° (compare Bülow and von Reden, Abstr., 1899, i, 150). When boiled with 70 per cent. sulphuric acid, the ester is hydrolysed to 3 : 3'-diphenyldicarboxylic acid, which crystallises from nitrobenzene and melts at 356–357° (compare Griess, Abstr., 1888, 826, and Bülow and von Reden, *loc. cit.*). Methyl 4 : 4'-diphenyldicarboxylate was prepared from methyl *p*-iodobenzoate and formed colourless leaflets melting at 214° (compare Weiler, Abstr., 1899, i, 490).

VIII. *Aldehyde Derivatives*.—4 : 4'-Dibenzylideneaniline,



was obtained by converting anhydroaminobenzaldehyde into *p*-iodobenzaldehyde (compare Hantzsch, Abstr., 1894, i, 331), which was then combined with aniline, forming *p*-iodobenzylideneaniline, a substance crystallising in colourless leaflets melting at 93°; when heated with copper at 260° and the product extracted with boiling benzene, the diphenyl derivative was obtained in colourless leaflets melting at 215°. 4 : 4'-Diphenyldialdehyde was prepared from dibenzylideneaniline by treatment with hot alcoholic hydrochloric acid, and crystallises in leaflets melting at 145°; the diphenylhydrazone, $\text{C}_{26}\text{H}_{22}\text{N}_4$, crystallises in yellow needles melting at 274°, and the dioxime, $\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_2$, forms pale brown crystals melting at 204°.

IX. *Ketone Derivatives*.—The preparation of 4 : 4'-dibenzoyldiphenyl, which crystallises in colourless leaflets melting at 218°, was effected as follows: by treatment of bromobenzene with magnesium in ethereal solution, a solution of magnesium phenyl bromide was obtained and then boiled with *p*-iodobenzaldehyde; the product was decomposed by adding it to ice-cold sulphuric acid, the volatile material removed by distilling in steam, and *p*-iodobenzhydrol,



extracted from the residue by petroleum; it forms colourless needles melting at 71° , and when oxidised with acetic acid and sodium dichromate is converted into *p*-iodobenzophenone (m. p. 102°) (compare Hofmann, Abstr., 1891, 1236). By heating the iodo-ketone with copper at 250° and extracting the product with benzene, the diphenyl derivative is isolated.

X. *Quinoline Derivatives*.—6-Iodoquinoline reacts violently with copper when they are heated together at 220° , the temperature rising to 340° ; from the product, 6:6'-diquinolyl can be extracted with alcohol; it crystallises in leaflets melting at 181° , whilst the diquinolyl, prepared from benzidine, melts at 178° .

XI. *Azo-derivatives*.—4:4'-Diphenylazodiphenyl is prepared by extracting with benzene the red product obtained by heating *p*-iodoazobenzene with copper at 250° ; it crystallises in orange-red, lustrous leaflets melting at 233.5° , and is probably identical with the substance (m. p. 226°) prepared by Bamberger (*Ber.*, 1896, 29, 103).

K. J. P. O.

2-Benzoylfluorene and Retene. MAX FORTNER (*Monatsh.*, 1904, 25, 443—452. Compare Abstr., 1903, i, 177).—2-Cyanofluorene, formed by the action of cuprous cyanide on 2-diazofluorene chloride (Diels, Abstr., 1901, i, 522), crystallises in yellow needles, melts at 88° , and is hydrolysed by concentrated hydrochloric acid with formation of fluorene-2-carboxylic acid. This crystallises in needles and sublimes with partial decomposition above 260° . The silver salt is a white, flocculent precipitate; the methyl ester crystallises in white needles and melts at 120° . Successive treatment of fluorene-2-carboxylic acid with thionyl chloride and with aluminium chloride and benzene leads to the formation of the benzoylfluorene, which was previously obtained by the action of benzoic chloride on fluorene in presence of aluminium chloride, and must be 2-benzoylfluorene,
$$\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{CH} \cdot \text{CH} \\ \text{CH}_2 - \text{C} \cdot \text{CH} \cdot \text{CBz} \end{array}$$
 On reduction,

2-benzoylfluorene yields 2-benzylfluorene, which is obtained by action of benzyl chloride on fluorene (Goldschmiedt, *Monatsh.*, 1881, 2, 443) or by reduction of fluorenylbenzoic acid (this vol., i, 168).

Oxidation of fluorene-2-carboxylic acid with sodium dichromate and glacial acetic acid leads to the formation of Bamberger and Hooker's diphenyleneketonecarboxylic acid (Abstr., 1885, 906, 1070). The methyl ester crystallises in glistening, yellow needles and melts at 181° . Retene must therefore be 2-methyl-8-propyl- or 8-methyl-2-propyl-phenanthrene.

G. Y.

Aniline-toluidine Oil from Caucasian Naphtha. W. N. OGLOBLIN (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 680—711).—The author has investigated two samples of aniline-toluidine oil prepared by Nikiforoff's patents from Russian naphtha; one sample contained aniline with a little *o*-toluidine and the other aniline with *o*-, *m*-, and *p*-toluidines.

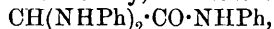
T. H. P.

ω -Cyanodimethylaniline. HANS BUCHERER (*Ber.*, 1904, 37, 2825. Compare Warunis and Sachs, this vol., i, 669).— ω -Cyanodimethyl-

aniline is prepared from sodium hydroxymethylenesulphonate, monomethylaniline, and potassium cyanide. A. McK.

Action of Dichloroacetic Acid on Aniline and the Tolidines. GUSTAV HELLER (*Annalen*, 1904, 332, 247—304).—The earlier work on the action of dichloroacetic acid on anilines, more especially on *o*-toluidine (Meyer, *Ber.*, 1883, 16, 925, 926, 2261) and on *p*-toluidine (Duisberg, *Abstr.*, 1885, 543), is discussed and an account given of the attempts, both analytical and synthetical, to ascertain the constitution of the products.

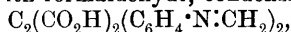
Action of Di- and Tri-halogen Substituted Anilides on Aromatic Bases.—[With RICHARD EMRICH.]—When dichloroaceto-*p*-toluidide (1 part) is heated on the water-bath with *p*-toluidine, the air having free access, *p*-methylisatin-*p*-tolylimide, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}:\overset{\text{CO}\cdot\text{NH}}{\underset{\text{C}_6\text{H}_4\text{Me}}{\text{C}}}$, is produced (compare Duisberg, *loc. cit.*). When aniline is caused to interact with dichloroacetanilide in the same way, dianilinoacetanilide,



is obtained as needles sintering at 137° and melting at 141—142°. Dichloroacetanilide and *o*-toluidine react in a similar manner, the product *di-o*-toluidinoacetanilide, $\text{C}_{22}\text{H}_{23}\text{ON}_3$, crystallising in needles melting at 166.5—167.5°. Dichloroacetanilide and *p*-toluidine yield a mixture of substances, one of which is slightly soluble and crystallises in needles melting at 262.5°; dichloroacetoluidide and aniline, on the other hand, give dianilidoacet-*p*-toluidide. Trichloroacet-*p*-toluidide (which melts at 113°, compare Judson, *Ber.*, 1870, 3, 784) and *p*-toluidine give a mixture of substances, which in any case contain no isatin, and from which, by means of alcohol, an insoluble crystalline substance, oxal-*p*-toluidide (m. p. 263°), $\text{C}_2\text{O}_2(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})_2$ (compare Hübner, *Annalen*, 1881, 209, 372) can be isolated. In a similar manner, trichloroacetanilide and aniline yield oxalanilide (m. p. 245°), no by-products being formed in this case. Trichloroacetanilide and *p*-toluidine yield phenyl-*p*-tolylloxamide, $\text{NHPh}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, which crystallises in four-sided plates melting at 206°, and is also produced, but with greater difficulty, from trichloroaceto-*p*-toluidide and aniline.

Action of Dichloroacetic Acid on Aniline.—[With RICHARD EMRICH.]—Mol. proportions of dichloroacetic acid as potassium salt and aniline were heated at 100° in aqueous solution in the presence of sodium acetate for five to six hours, when an oil separates. This material yields two isomerides, dibasic acids, $[\text{C}(\text{CO}_2\text{H})\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}]_2$; on extraction with hot 10 per cent. sodium acetate solution, the one separates from the cold sodium acetate solution, and the other only after acidifying; the former, the α -compound, crystallises from sodium acetate solution in pale yellow aggregates of microscopic crystals, whilst the β -compound, which also forms microscopic crystals, is distinguished from the α -compound by its different behaviour towards solutions of sodium acetate, in which it is more soluble, and towards dilute acids; the salts of both acids are similar and not characteristic; both acids become coloured at 270°, sinter, and then decompose. The α -acid is converted into the β -compound by dissolving in potassium hydroxide, the change beginning after one of the carboxyl groups is

neutralised. When either the α - or the β -compound is kept, partial transformation occurs. Both the α - and β -compounds give, in hydrochloric acid solution with formaldehyde, condensation products,



which in both cases form insoluble crystalline aggregates, decomposing at a high temperature. *Compounds* with salicylaldehyde, $\text{C}_{30}\text{H}_{22}\text{O}_6\text{N}_2$, have also been prepared as amorphous insoluble powders, decomposing on heating. The *acetyl* derivative, prepared from the β -acid, is crystalline. Both the α - and the β -acids can be diazotised, but the α -compound only with difficulty.

The *aniline* salt of anilinoxylic acid, $\text{NPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}\cdot\text{NH}_2\text{Ph}$, is formed either when a concentrated aqueous solution of glyoxylic acid is treated with aniline acetate, or when potassium dichloroacetate is heated in aqueous solution with potassium acetate and aniline acetate (compare Doebner, *Abstr.*, 1900, i, 473); it crystallises in slender, white needles melting at $92-93^\circ$, and is immediately decomposed by acids and alkalis; all attempts to prepare an acid from this salt resulted in the α -acid just described.

Synthesis of Stilbene Derivatives.—[With KARL AMBERGER.]—4:4'-*Dinitrodiacyanostilbene*, $\text{C}_2(\text{CN})_2(\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$, is prepared by adding to a solution of *p*-nitrobenzyl cyanide in methyl alcohol a solution of iodine in absolute ether and a solution of sodium methoxide in methyl alcohol; it crystallises in microscopic prisms melting at $268-269^\circ$, and dissolves in a solution of sodium methoxide with an intense violet coloration. On reduction with a solution of stannous chloride, it is converted into the corresponding *diamino*-compound, which crystallises in small plates or needles melting over 300° , when it also sublimes. 4:4'-*Dinitrostilbenedicarboxylic anhydride* is prepared from the diacyanide by hydrolysis in acetic acid solution by means of hydrochloric acid under pressure at $185-190^\circ$; it crystallises in needles or quadratic plates melting at 197° . 4:4'-*Diaminostilbenedicarboxylic acid*, prepared by reducing the dinitro-compound with ammonium sulphide, forms intensely red flocks.

2:2'-*Dinitrodiacyanostilbene*, prepared in the same manner as the para-compound from *o*-nitrobenzyl cyanide, crystallises in needles, becoming coloured at 210° and decomposing at 265° ; on reduction, the 2:2'-*diaminodicyanostilbene* is obtained as an insoluble solid, melting and decomposing at 265° ; it could not be hydrolysed. 2:2'-*Dinitrostilbenedicarboxylic acid* can only be prepared by hydrolysis of the dinitro-compound in acetic acid solution with hydrochloric acid, when the acid amide is produced; this substance is converted into the acid by boiling with dilute sodium hydroxide; the acid sinters at 232° and melts and decomposes at 237.5° .

The connection between molecular vibrations and those due to chemical reactions is discussed at length. K. J. P. O.

Elimination of Alkyl Groups from Secondary Amines. JULIUS VON BRAUN (*Ber.*, 1904, 37, 2812—2819).—The secondary amine, NHR_2 , is converted first of all into the dialkylated amide, $\text{R}_1\cdot\text{CO}\cdot\text{NR}_2$. In the event of R_1 in this latter type containing a benzene, substituted benzene, or a naphthalene residue, the amide is

converted into the amide chloride, $R_1 \cdot CCl_2 \cdot NR_2$, which, when heated, undergoes decomposition in two stages, namely: (1) $R_1 \cdot CCl_2 \cdot NR_2 = R_1 \cdot CCl : NR + RCl$ and (2) $R_1 \cdot CCl_2 \cdot NR_2 = R_1 \cdot CN + 2RCl$, the latter reaction taking place at the more elevated temperature. When one of the alkyl groups attached to the nitrogen atom is aromatic, however, the reaction is confined to the first stage, one molecule of aliphatic alkyl chloride being eliminated, whilst the imide chloride, $R \cdot CCl : NR$ (where R is an aromatic group), remains, as such compounds are not decomposed by heat at relatively high temperatures. Since, accordingly, imide chlorides are converted by water into monalkylated amides, $R_1 \cdot CO \cdot NHR$, which, on further hydrolysis, yield primary bases NH_2R , and since nitriles can be hydrolysed to ammonia, the reactions described by the author provide a method for converting a secondary amine, NHR_2 , into a primary amine, NH_2R , and into ammonia.

Dimethylbenzamide, $COPh \cdot NMe_2$, reacts vigorously with phosphorus pentachloride at about 110° ; methyl chloride is evolved, whilst the residue contains methylbenzimidochloride, $CPhCl : NMe$, boiling at $80-105^\circ$ under 10 mm. pressure (the boiling point is not sharp, since a little benzonitrile is always present). By the action of water on the imide chloride, methylbenzamide, $COPh \cdot NHMe$, boiling at 167° under 11 mm. pressure, is formed.

When the action of phosphorus pentachloride on dimethylbenzamide is completed at $160-170^\circ$, the action proceeds further, a second molecule of methyl chloride being eliminated and benzonitrile being formed along with its polymerisation product, cyaphenin.

Diethylbenzamide, $COPh \cdot NEt_2$, is converted in an analogous manner into ethylbenzamide, $COPh \cdot NHEt$, which melts at 67° . Benzonitrile and cyaphenin are obtained where the action is conducted at a higher temperature.

Phenylmethylbenzamide, $COPh \cdot NMePh$, is converted similarly into the corresponding imide chloride, then into the amide, which, on hydrolysis, yields aniline.

Phenylbenzylbenzamide, $COPh \cdot NPh \cdot C_7H_7$, when similarly treated, yielded benzanilide and benzyl chloride.

Dimethyl-p-bromobenzamide, $C_6H_4Br \cdot CO \cdot NMe_2$, prepared by the action of *p*-bromobenzoyl chloride on dimethylamine, separates from ether in glistening crystals and melts at 72° ; when heated with phosphorus pentachloride at 170° , it forms *p*-bromobenzonitrile.

Dimethyl- α -naphthylamide, $C_{10}H_7 \cdot CO \cdot NMe_2$, when similarly treated, yields α -naphthonitrile.

A. McK.

Isomerism of Asymmetric Tolylammonium Salts. EDGAR WEDEKIND and F. OBERHEIDE (*Ber.*, 1904, 37, 2712—2727. Compare Abstr., 1902, i, 277, 643; 1903, i, 517; this vol., i, 37).—*Methyl-ethyl-p-toluidine* is a pale yellow oil distilling at $218-220^\circ$; the *picrate* crystallises in yellow needles and melts at 78° . The base combines readily with allyl iodide yielding *p-tolylmethylethylallyl-ammonium iodide*, which crystallises from chloroform in colourless needles containing a molecule of chloroform and melting and decomposing at $140-142^\circ$.

Ethylallyl-p-toluidine, $C_6H_4Me \cdot NEt \cdot C_3H_5$, distils at 238° and its *picrate* crystallises in lemon-yellow needles melting at 111° . The base combines with methyl iodide, forming a vitreous mass which slowly crystallises. When the crude product is crystallised from chloroform, the compound melting and decomposing at $140-142^\circ$ is obtained, which crystallises in rhombic prisms [$a : b : c = 0.8209 : 1 : 0.7549$]

p-Tolylmethylethylallylammonium bromide crystallises from a mixture of benzene and chloroform in colourless, monoclinic needles decomposing at $173-174^\circ$.

The *nitrate* crystallises from chloroform in large, colourless needles containing a molecule of chloroform and melting at $95-97^\circ$. The *d-camphorsulphonate* forms hygroscopic needles melting at $160-161^\circ$, and could not be resolved by fractional crystallisation from a mixture of acetone and ethyl acetate.

Methylallyl-p-toluidine is a colourless oil distilling at $230-232^\circ$; the *picrate* crystallises from alcohol in yellowish-brown needles melting at 124° . The base readily combines with benzyl iodide, yielding *benzyl-p-tolylmethylethylallylammonium iodide*, which is deposited from a mixture of alcohol and ether in colourless crystals melting at $144-146^\circ$.

Allyl-p-toluidine, obtained by the action of allyl iodide on sodium formotoluide and subsequent hydrolysis with concentrated hydrochloric acid, and purified by conversion into its nitroso-derivative, is an oil distilling at $232-234^\circ$. The *hydrochloride* melts at $131-132^\circ$ and the *acid oxalate* at $150-151^\circ$. On treatment with benzyl iodide, the base is converted into *benzylallyl-p-toluidine*, which distils at $214-215^\circ$ under 31 mm. pressure. The *picrate* crystallises from alcohol in lemon-yellow needles melting at 138° . The tertiary base combines with methyl iodide yielding the quaternary ammonium iodide which decomposes at $144-146^\circ$. This same compound is also formed by the union of allyl iodide and benzylmethyl-p-toluidine (Rabaut, Abstr., 1892, 313). Benzyl-p-tolylmethylethylallylammonium iodide crystallises from alcoholic solutions in triclinic prisms [$a : b : c = 0.7686 : 1 : 0.8663$; $\alpha = 88^\circ 37'$; $\beta = 105^\circ 18\frac{1}{2}'$; $\gamma = 84^\circ 5'$]; it separates from aqueous solutions in triclinic crystals of somewhat different form. The corresponding *bromide* forms colourless needles melting and decomposing at $146-147^\circ$; the *nitrate* decomposes at $134-136^\circ$, and the *d-camphorsulphonate* melts at $167-168^\circ$. No resolution by fractional crystallisation has been effected.

Benzyl iodide combines with ethylallyl-p-toluidine, yielding a crystalline *benzyl-p-tolylethylallylammonium iodide*, which crystallises from absolute alcohol in colourless needles decomposing at $114-116^\circ$.

Benzylethyl-p-toluidine distils at 226° under 26 mm. pressure as a viscid, yellow oil and yields a *picrate* melting at 138° . It combines slowly with allyl iodide, yielding an amorphous, quaternary salt.

J. J. S.

Benzenesulphonylcyanamides of Primary Bases. JULIUS VON BRAUN (*Ber.*, 1904, 37, 2809-2812).—Although benzenesulphonylcyananilide is produced in a good yield by interaction of benzenesulphonanilide and cyanogen bromide in the presence of alkali, thus: $Ph \cdot SO_2 \cdot NPhNa + BrCN = NaBr + Ph \cdot SO_2 \cdot NPh \cdot CN$, the yield is not

always good in reactions of a similar type. The method cannot accordingly be employed as a general one for the purification of primary bases by converting the latter into cyanobenzenesulphonamides and then hydrolysing these.

Benzenesulphoncyanoanilide, $\text{Ph}\cdot\text{SO}_2\cdot\text{NPh}\cdot\text{CN}$, prepared from the sodium salt of benzenesulphonanilide and cyanogen bromide, melts at $66-67^\circ$.

Benzenesulphoncyano-p-toluidide, $\text{Ph}\cdot\text{SO}_2\cdot\text{N}(\text{C}_6\text{H}_4\text{Me})\cdot\text{CN}$, melts at 88° .

Benzenesulphoncyano-p-anisidide, $\text{Ph}\cdot\text{SO}_2\cdot\text{N}(\text{C}_6\text{H}_4\cdot\text{OMe})\cdot\text{CN}$, melts at $95-96^\circ$.

Benzenesulphoncyanomethylamide, $\text{Ph}\cdot\text{SO}_2\cdot\text{NMe}\cdot\text{CN}$, boils at 205° under 30 mm. pressure and melts at $45-46^\circ$.

Benzenesulphoncyanoethylamide boils at 195° under 15 mm. pressure.

o-Chlorobenzenesulphonanilide separates from alcohol in spear-shaped crystals and melts at 127° .

The cyanogen group in the amides described is very readily removed during hydrolysis.

A. McK.

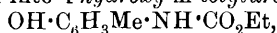
Action of a Trace of Certain Salts or of Alkali Hydroxides on Phenyl Carbonate. ROBERT FOSSE (*Compt. rend.*, 1904, 139, 141-143).—The trace of sodium carbonate which at $200-300^\circ$ determines the conversion of phenyl carbonate into carbon dioxide, phenol, and phenyl *o*-phenoxybenzoate (compare Abstr., 1903, i, 485) can be replaced by sodium phosphate, arsenate, di- or tetra-borate, sodium or potassium hydroxide, sodium salicylate or ethoxide. The action of large quantities of sodium ethoxide or hydroxide on phenyl carbonate has been examined by Hentschel (compare Abstr., 1883, 589), who obtained sodium salicylate and phenetole in the first case, and sodium salicylate and phenol in the second.

M. A. W.

Molecular Rearrangement of Aminophenyl Alkyl Carbonates. HENRY T. UPSON (*Amer. Chem. J.*, 1904, 32, 13-43. Compare Stieglitz and Upson, this vol., i, 575).—*p*-Nitrophenyl methyl carbonate, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}_2\text{Me}$, obtained by the action of methyl chlorocarbonate on *p*-nitrophenol in alkaline solution, is a white, solid substance which melts at $111-112^\circ$ and is soluble in ether or alcohol. When treated with stannous chloride and hydrochloric acid, it is converted into the hydrochloride of *p*-aminophenyl methyl carbonate, which, when left in water for several hours, shows no tendency to undergo molecular rearrangement. *o*-Nitrophenyl methyl carbonate is a yellow, mobile oil. The hydrochloride of *o*-aminophenyl methyl carbonate forms a white solid.

3-Nitro-p-tolyl ethyl carbonate, $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{O}\cdot\text{CO}_2\text{Et}$, crystallises from alcohol and melts at 56° . By reducing this compound with tin and hydrochloric acid and subsequently boiling the solution, a mixture of 4-hydroxy-*m*-tolylurethane and carbonyl *o*-amino-*p*-cresol is produced. If, however, the reduction is effected in the cold, and, after the addition of alkali, the product is extracted with ether and the ethereal solution is treated with dry hydrogen chloride, the hydrochloride of 3-amino-*p*-tolyl ethyl carbonate is obtained as a white precipitate which melts

and decomposes at 135—137°; the *platinichloride* melts and decomposes above 171°. When the hydrochloride is dissolved in water, it is gradually converted into 4-hydroxy-m-tolylurethane,



which melts at 101°. *Carbonyl-3-amino-p-cresol*, $\text{C}_6\text{H}_3\text{Me}\begin{smallmatrix} \text{---O---} \\ \text{NH} \end{smallmatrix}\text{CO}$, crystallises in white needles, melts at 128°, and is soluble in alcohol, ether, or chloroform.

4-Nitro-m-tolyl ethyl carbonate, obtained from 4-nitro-m-cresol, is a yellow oil which solidifies at -5°. The *hydrochloride* and *platinichloride* of 4-amino-m-tolyl ethyl carbonate were prepared; the aqueous solution of the hydrochloride deposits crystals of 3-hydroxy-p-tolylurethane, $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, which melts at 95° and is soluble in alcohol, ether, or chloroform.

6-Nitro-o-tolyl ethyl carbonate crystallises in yellow needles and melts at 32—33°. The *hydrochloride* of 6-amino-o-tolyl ethyl carbonate is very soluble in water; the *platinichloride* was prepared and analysed. 2-Hydroxy-m-tolylurethane, which gradually separates from an aqueous solution of the hydrochloride, crystallises in white needles, melts at 74—76°, and is soluble in alcohol or ether.

4-Chloro-2-nitrophenyl ethyl carbonate forms nearly white crystals and melts at 60°. The *hydrochloride* of 4-chloro-2-aminophenyl ethyl carbonate, $\text{CO}_2\text{Et}\cdot\text{O}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{NH}_2\cdot\text{HCl}$, is obtained as a white solid and is insoluble in water; the *platinichloride* crystallises in yellow needles. When the hydrochloride is boiled with water, it is converted into 3-chloro-6-hydroxyphenylurethane, $\text{OH}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, which forms white needles and melts at 136—137°; this compound is also obtained by the action of ethyl chloroformate on 4-chloro-2-aminophenol. If the urethane is heated for some time at 230°, it is decomposed with formation of *carbonyl-4-chloro-2-aminophenol*, which crystallises in white needles and melts at 184—185°.

6-Chloro-2-nitrophenyl ethyl carbonate was obtained as an oil which did not solidify when cooled to -15°. The *hydrochloride* of 6-chloro-2-aminophenyl ethyl carbonate melts and decomposes at 126—127°, and is soluble in alcohol, but insoluble in water. When heated with water, it is converted into 5-chloro-6-hydroxyphenylurethane, which crystallises in needles and melts at 92—93°.

4-Bromo-2-nitrophenyl ethyl carbonate crystallises from ether in large, transparent plates and melts at 76°. The *hydrochloride* of 4-bromo-2-aminophenyl ethyl carbonate melts at 136—137°. 3-Bromo-6-hydroxyphenylurethane crystallises in white needles and melts at 140—142°.

4 : 6-Dichloro-2-nitrophenyl ethyl carbonate is a yellow solid which melts at 38—39°. The *hydrochloride* of 4 : 6-dichloro-2-aminophenyl ethyl carbonate melts and decomposes at 132—135° and is soluble in alcohol but insoluble in water; it is readily converted into 3 : 5-dichloro-6-hydroxyphenylurethane, which melts at 125° and may also be obtained by the action of ethyl chloroformate on 4 : 6-dichloro-2-aminophenol.

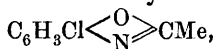
4-Chloro-6-bromo-2-nitrophenyl ethyl carbonate crystallises in yellow prisms and melts at 48—49.5°. The *hydrochloride* of 4-chloro-6-bromo-2-aminophenyl ethyl carbonate melts and decomposes at 131—132° and

is insoluble in water. 3 *Chloro-5-bromo-6-hydroxyphenylurethane* melts at 116—118°.

5-*Bromo-3-nitro-o-tolyl ethyl carbonate* melts at 61—62° and is soluble in alcohol, ether, or chloroform. The *hydrochloride* of 5-bromo-3-amino-o-tolyl ethyl carbonate is soluble in alcohol and insoluble in water, darkens at 137—143°, and melts and decomposes at 173—178°. 5-*Bromo-2-hydroxy-m-tolylurethane* melts at 123°.

5-*Bromo-3-nitro-p-tolyl ethyl carbonate* melts at 84—85°. The *hydrochloride* of 5-bromo-3-amino-p-tolyl ethyl carbonate melts and decomposes at 142—143° and is insoluble in water. 5-*Bromo-4-hydroxy-m-tolylurethane* melts at 83° and is soluble in alcohol or ether.

4-*Chloro-2-nitrophenyl acetate*, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{OAc}$, obtained by the action of acetic anhydride on 4-chloro-2-nitrophenol, melts at 47—48° and is readily soluble in benzene, chloroform, or ether, and fairly so in alcohol. On reduction with tin and hydrochloric acid, it is converted into the *hydrochloride* of 4-chloro-2-aminophenyl acetate, which melts at 105—107°; the *platinichloride* darkens at 120° and remains unmelted at 200°. 4-*Chloro-2-aminophenyl acetate*, $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{OAc}$, crystallises in white needles and melts at 73—74°; if left for a day, it undergoes molecular rearrangement with formation of *acetyl-4-chloro-2-aminophenol*, $\text{NHAc} \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{OH}$, which melts at 176° and may also be prepared by the action of acetic anhydride on 4-chloro-2-aminophenol. When *acetyl-4-chloro-2-aminophenol* is heated at 220°, it is converted into 4-chloro-2-ethenylaminophenol,



which crystallises in white needles, melts at 53—54°, has a peculiar, pleasant odour, and is soluble in ether, alcohol, benzene, or chloroform; its *hydrochloride* melts at 129—130.5°; the *platinichloride* is also described. E. G.

Molecular Transformation of Acylated Aminohydroxy-compounds. KARL AUWERS (*Annalen*, 1904, 332, 159—213).—In the course of an investigation of the phenol bromides, it was observed that when bases acted on acetyl derivatives of phenols of the type $\text{C}_6\text{X}_4(\text{OAc}) \cdot \text{CH}_2\text{Br}$, the acetyl and the substituted methyl groups being in the ortho-position relative to one another, the bromine atom was not only replaced by the base, but the acetyl group wandered from the oxygen to the nitrogen, thus:

$\text{OAc} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{CH}_2\text{Br} + \text{NH}_2\text{Ph} \rightarrow \text{OH} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{CH}_2 \cdot \text{NPhAc}$,
a reaction which takes place in benzene solution either at 100° or at the ordinary temperature.

This change has only been observed in the case of *o*-hydroxybenzyl compounds, but not with the isomeric *m*- and *p*-derivatives. Investigation of the influence of the nature of the base or the acyl group on the tendency of the *o*-hydroxybenzyl compounds to undergo this transformation appears to show that the change is not dependent on these factors. The part played by the base was more particularly investigated; all the substituted anilines behave like aniline itself; the bases of the fatty series act in the same way, but still more readily; this increased activity is not due merely to their being stronger bases,

since the weaker bases effect a similar change. Whether the weakest bases (so far as they are still capable of being acetylated) are capable of producing the change cannot be decided, since they are not able to form condensation products with the brominated *ψ*-phenols. It has not been experimentally demonstrated that the acyl group should possess a certain definite degree of acid character in order that the transformation should occur; but since the course of the reaction appears to be independent of the strength of the base, and since even the radicle of carbonic acid can be made to wander from the oxygen to the nitrogen, it would seem that the transformation is independent also of the chemical nature of the acyl group. The mass (mol. volume) of the acyl group has no influence on the change.

No thorough attempt has up to the present been made to ascertain how far steric influences hinder or otherwise affect the transformation in the case of *o*-hydroxybenzyl derivatives. All experiments having as their object the isolation of the supposed primary product of the reaction $C_6X_4(OAc) \cdot CH_2 \cdot NPh$ (low temperatures being used during the whole of the operations), led to no result; in all cases, the product of the transformation was alone obtained; the *O*-ester is extremely labile, even if it is capable of existence.

Since it was possible that the esters of aliphatic amino-alcohols would behave towards bases as the esters of *o*-hydroxybenzyl derivatives, the action of aniline on the benzoate of ethylenebromohydrin was investigated; the reaction, which took place even at a high temperature, is represented thus: $CH_2Br \cdot CH_2OBz + 2NH_2Ph = NPh \cdot CH_2 \cdot CH_2 \cdot OBz + NH_2Ph \cdot HBr$; no wandering of the acyl group was detected. The *O*-esters of the amino-alcohols, which have mainly been investigated in the form of their salts, are stable and do not change when boiled with dilute acids. It has not yet been ascertained whether the *N*-ester of the amino-alcohols, which is also stable under ordinary conditions, can be transformed into the *O*-ester; nor is it known whether an amino-alcohol, in acylation, is converted first into an *O*- or an *N*-ester.

The aromatic are quite similar to the aliphatic alcohols, both *N*- and *O*-esters being capable of existence and not directly transformable the one into the other. If the formulæ of the stable *O*-ester of *o*-amino-benzylalcohol and of the unstable derivative of *o*-hydroxybenzylamine are compared, $-C(N \equiv) \cdot C \leq CH_2 \cdot O-$ and $-C(O-) \cdot C \leq CH_2 \cdot N \equiv$,

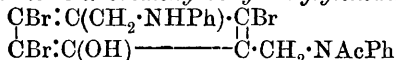
it is seen that the distance between the oxygen and nitrogen atoms is not materially different in the two compounds. The cause of the difference of behaviour is therefore not to be found in different spacial relations. It is suggested that the only grounds for the difference in stability of the *O*-esters of amino-alcohols on the one hand, and of *o*-hydroxybenzylamines on the other, are to be sought in the fact that the union of the alcoholic oxygen with the acyl group is more powerful than that of the phenolic oxygen; in the latter case, therefore, the attraction of the basic amino-group is sufficiently powerful to bring about the intramolecular change.

I. *Action of Aniline on Acetyl Derivatives of Substituted o-, m-, and p-Hydroxybenzyl Bromides.*—[With OTTO ANSELMINO and W. RICHTER.]

—The aniline (2 mols.) and the acetate (1 mol.), which was being studied, were heated together in benzene solution on the water-bath until the amount of aniline hydrobromide which separated no longer increased. The benzene was evaporated and the anilide isolated in various ways. By the behaviour of the product towards alkalis, it could generally be ascertained whether the acetyl group had wandered to the nitrogen, or the primary product could be converted into a diacetyl derivative by boiling with acetic anhydride, which is then hydrolysed, the identity of the resulting *N*-ester of the hydroxybenzylaniline with the initial product of the reaction showing that the acetyl group had migrated; finally, the constitution of the product could be demonstrated by condensing the original ψ -phenol, instead of its acetyl derivative, with aniline and then acetylating in the cold, when only the *N*-ester is formed and can be compared with the product of the reaction of the acetyl derivative with aniline.

A. *Ortho-compounds*.—The *N*-acetate of 3:5-dibromo-*o*-hydroxybenzylaniline, $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{NAcPh}$, obtained from dibromo-*o*-acetoxybenzyl bromide and aniline by the action of acetic anhydride on dibromo-*o*-hydroxybenzylaniline in the cold or by hydrolysis with alcoholic sodium hydroxide of the diacetyl compound, crystallises in needles melting at 152° . The *N*-acetate of 2:3:4:5-tetrabromo-*o*-hydroxybenzylaniline, prepared from tetrabromo-*o*-acetoxybenzyl bromide and aniline, and also obtained by partial hydrolysis of the diacetate of tetrabromo-*o*-hydroxybenzylaniline, or by the acetylation in the cold of tetrabromo-*o*-hydroxybenzylaniline, crystallises in flattened needles or in lustrous prisms melting at 157 – 158° ; the corresponding phenol, $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_4\cdot\text{CH}_2\cdot\text{NHPh}$, prepared by the action of aniline (2 mols.) on tetrabromo-*o*-hydroxybenzyl bromide (1 mol.) in benzene solution, forms needles which begin to decompose at 165° and are completely molten at 170° ; the diacetyl derivative crystallises in rhombic leaflets melting at 161 – 162° .

The *N*-monoacetate of tribromohydroxy-*m*-xylylenedianiline,



(compare Abstr., 1900, i, 97), melts at 209° , has the constitution represented by the formula, and is formed when aniline interacts with 3:4:6-tribromo-2-acetoxy-*m*-xylylene bromide, the acetyl group wandering from the oxygen to the nitrogen. A similar change was observed when aniline acts on 3:5:6-tribromo-2-acetoxy-*p*-xylylene bromide.

B. *Meta-compounds*.—The *O*-acetate of 2:4:6-tribromo-*m*-hydroxybenzylaniline, $\text{OAc}\cdot\text{C}_6\text{HBr}_3\cdot\text{CH}_2\cdot\text{NHPh}$, prepared by the action of tribromo-*m*-acetoxybenzyl bromide (1 mol.) with aniline (2 mols.), forms crystals melting at 99 – 100° , and by hydrolysis with alcoholic potassium hydroxide is converted into tribromo-*m*-hydroxybenzylaniline, which crystallises in needles melting at 96° . When the latter is treated with cold acetic anhydride, the isomeric *N*-acetate is obtained, crystallising in prisms melting at 180° . The product obtained from dibromo-*m*-acetoxy- ψ -cumyl bromide and aniline is probably an *O*-acetate, since it is insoluble in alkali hydroxides.

C. *Para-compounds*.—The *O*-acetate of 3:6-dibromo-*p*-hydroxy- ψ -

cumylaniline, $\text{OAc} \cdot \text{C} \begin{smallmatrix} \text{CMe} \cdot \text{CBr} \\ \text{CBr} \cdot \text{CMe} \end{smallmatrix} \text{C} \cdot \text{CH}_2 \cdot \text{NHPh}$, prepared from the acetyl derivative of dibromo- ψ -cumenol bromide and aniline in benzene solution, melts at 120° ; the *N*-acetate (m. p. $223\text{--}225^\circ$), obtained by the action of acetic anhydride on the base, is easily converted into the *diacetate* by boiling with acetic anhydride, which crystallises in needles or lustrous prisms melting at 140° ; by digestion with alcoholic potassium hydroxide, the *N*-acetate is regenerated. A similar *O*-acetate, which is insoluble in alkali hydroxides, is obtained by the action of aniline on the acetyl derivative of 3:5:6-tribromo-4-hydroxy-*o*-xylylene bromide.

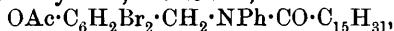
II. *Reaction of Dibromo-*o*-acetoxybenzyl Bromide with Primary Bases.*—[With H. ULRICH.]—The investigation of a number of primary bases, many of them with negative substituents, showed that they behaved in the same manner as aniline. The *N*-acetate of 3:5-dibromo-*o*-hydroxybenzyl-*o*-toluidine, prepared from dibromo-*o*-acetoxybenzyl bromide (1 mol.) and *o*-toluidine (2 mols.) in benzene solution, crystallises in small needles melting at 115° . The corresponding derivative of β -naphthylamine, which was prepared in similar manner, forms small needles melting at 137° , and the *N*-acetate, obtained by the use of amylamine, in silky needles melting at 150° .

The *N*-acetate of 3:5-dibromo-*o*-hydroxybenzyl-*o*-chloroaniline, obtained by the use of *o*-chloroaniline, forms short prisms melting at $129\text{--}130^\circ$, and the corresponding compound from 2:4-dichloroaniline stellate groups of needles melting at $141\cdot5\text{--}143\cdot5^\circ$. The *N*-acetate of 3:5-dibromo-*o*-hydroxybenzyl-*m*-nitroaniline, prepared from dibromoacetoxybenzyl bromide and *m*-nitroaniline in alcoholic solution at 100° , forms yellow crystals melting at $158\text{--}159^\circ$, and the corresponding compound from *p*-nitroaniline yellow rhombohedra or prisms melting at 146° . *o*-Nitroaniline, 2:4-dinitroaniline, and 3-nitro-4-toluidine will not condense with the dibromoacetoxybenzyl bromide.

The *N*-acetate of 3:5-dibromo-*o*-hydroxybenzyl-5-nitro-*o*-toluidine, prepared in the usual manner, crystallises in lustrous needles or monoclinic prisms melting at $161\text{--}162^\circ$; the corresponding compound from 2-nitro-*p*-toluidine crystallises in yellow, rectangular plates melting at $179\text{--}180\cdot5^\circ$. The *N*-acetate of 3:5-dibromo-*o*-hydroxybenzyl-*o*-anisidine, crystallises in prisms melting at $102\text{--}103^\circ$, and the compound from *p*-anisidine in star-shaped groups of needles melting at $114\text{--}115^\circ$. The *N*-acetate of 3:5-dibromo-*o*-hydroxybenzylanthranilic acid is obtained in the usual manner or by acetylating the base, 3:5-dibromo-*o*-hydroxybenzylanthranilic acid, which is obtained from dibromo-*o*-hydroxybenzyl bromide and anthranilic acid and forms transparent rhombohedra melting at $175\text{--}178^\circ$; the acetate crystallises in monoclinic prisms melting at $201\text{--}202^\circ$. The acetate, prepared from *m*-aminobenzoic acid, crystallises in small cubes melting at 213° . 3:5-Dibromo-*o*-hydroxybenzyl-*m*-aminobenzoic acid, prepared from *m*-aminobenzoic acid and dibromohydroxybenzyl bromide, forms crystals melting indefinitely at 167° , and on acetylation is converted into the derivative just described. Methyl 3:5-dibromo-*o*-hydroxybenzyl-*m*-aminobenzoate, prepared from dibromohydroxybenzyl bromide and methyl *m*-aminobenzoate, crystallises in small needles or prisms melting at $120\text{--}123^\circ$; on

acetylation, it yields the *N*-acetate of methyl dibromohydroxybenzyl-*m*-aminobenzoate, which can also be obtained from dibromohydroxybenzyl bromide and methyl *m*-aminobenzoate, and crystallises in groups of needles melting at 117—119°. The *N*-acetate of 3 : 5-dibromohydroxybenzyl-*p*-aminobenzoic acid crystallises in transparent cubes melting at 221—222°. The *N*-acetate of 3 : 5-dibromohydroxybenzyl- ψ -cumidine crystallises in needles or prisms melting at 120—121°.

III. *Migration of Heavy Acidic Radicles*.—[With E. BERGS and FRITZ WINTERNITZ.]—In the reaction of the benzoic, lauric, and palmitic esters of dibromo-*o*-hydroxybenzyl bromide with aniline, the acyl group wanders from the oxygen to the nitrogen just as the acetyl group migrates in the acetates. 3 : 5-Dibromo-*o*-benzoxybenzyl bromide, $\text{OBz} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{CH}_2\text{Br}$, prepared by benzoylating dibromo-*o*-hydroxybenzyl bromide with benzoyl chloride, crystallises in needles melting at 119—120° and reacts with aniline (2 mols.) in ethereal solution forming the *N*-benzoate of dibromobenzylaniline, which forms scales melting at 163°. The laurate of 3 : 5-dibromo-*o*-hydroxybenzyl bromide, $\text{CH}_2\text{Br} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{C}_{11}\text{H}_{23}$, prepared by heating under reduced pressure mol. quantities of lauryl chloride and dibromo-*o*-hydroxybenzyl bromide, crystallises in needles melting at 60—61° and is converted by boiling with aniline into the *N*-laurate of dibromohydroxybenzylaniline, which forms white needles melting at 50—51°. The palmitate of dibromohydroxybenzyl bromide crystallises in white needles melting at 75°, and the *N*-palmitate of the benzylaniline, obtained from it, in needles melting at 56—57°; on boiling the latter with acetic anhydride, the acetate,



is obtained in crystalline form melting at 64—65°, and readily converted by alcoholic potassium hydroxide into the *N*-palmitate.

Experiments on the reduction of the *o*-nitrophenyl esters of acids of heavy mol. weight, made with the object of ascertaining whether the *O*-ester was formed, or whether it changed into the *N*-ester, gave no distinct results, since in all cases mixtures, which could not be separated, were formed.

o-Nitrophenyl laurate, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CO} \cdot \text{C}_{11}\text{H}_{23}$, prepared by the interaction of mol. quantities of lauryl chloride and *o*-nitrophenol in solution in pyridine, crystallises in monoclinic prisms melting at 35—36°; the palmitate forms small needles melting at 51—52° and the stearate melts at 60—61°. The *N*-lauryl derivative of *o*-aminophenol, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_{11}\text{H}_{23}$, prepared by the action of lauryl chloride on *o*-aminophenol in acetone solution, crystallises in leaflets of a pale rose colour, melting at 68—69°, and the corresponding palmitate in leaflets melting at 78—79°.

IV. *Experiments with Amino-alcohols*.—[With E. BERGS.]—The interaction of aniline and the acetate and benzoate of ethylenebromohydrin was investigated. In the case of the benzoate, even at a temperature of 140—150°, the benzoate of β -hydroxyethylamine, $\text{NHPh} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{COBz}$, was quantitatively formed, no migration of the benzoyl group being observed. In the case of the acetate, on the other hand, both the bromine and the acetyl group were replaced

by anilino-groups, the acetyl derivative of symmetrical diphenyl ethylenediamine, $\text{NPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NAcPh}$, being produced.

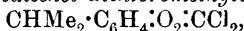
The *benzoate* of ethylenebromohydrin, $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{O}\cdot\text{COBz}$, prepared by warming mol. quantities of ethylenebromohydrin and benzoyl chloride at 100° , is a clear liquid boiling at $147\text{--}149^\circ$ under 15 mm. and at $280\text{--}285^\circ$ with decomposition under the ordinary pressure; when warmed with aniline (2 mols.), it is converted into β -benzoxyethyl-aniline, crystallising in needles melting at 77° ; the *hydrochloride* forms needles melting at 130° ; the *nitroso*-derivative is a greenish-yellow oil, decomposing on warming. The *dibenzoate* of β -hydroxyethyl-aniline, $\text{NPhBz}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{COBz}$, prepared from the monobenzoate and benzoyl chloride, crystallises in needles melting at $91\text{--}92^\circ$, and by partial hydrolysis with alcoholic potassium hydroxide is converted into the *N-benzoate*, $\text{NPhBz}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, which crystallises in needles melting indefinitely at $142\text{--}146^\circ$. This compound could not be obtained by heating the isomeric *O*-benzoate in benzene solution at $160\text{--}180^\circ$.

When the acetate of ethylenebromohydrin is heated with aniline at $140\text{--}150^\circ$, or in benzene solution for 8–10 hours, the acetyl derivative of diphenylethylenediamine (m. p. 128°) is produced, and can be converted into the diacetyl derivative (m. p. 158°) by boiling with acetic anhydride.

K. J. P. O.

Two Homologues of Catechol. RAYMOND DELANGE (*Compt. rend.*, 1904, 138, 1701–1703. Compare Abstr., 1900, i, 289).—*Ethylcatechol*, obtained from ethylcatechol methylene ether (compare Klages, this vol., i, 46) by converting it into ethylcatechol dichloromethylene ether, $\text{CCl}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}_4\text{Et}$, boiling at $133\text{--}135^\circ$ under 20 mm. pressure, by the action of phosphorus pentachloride, and boiling this compound with water, boils at $157\text{--}160^\circ$ under 19 mm. pressure, is very soluble in water or the ordinary organic solvents, sparingly soluble in light petroleum ($30\text{--}60^\circ$), from which it crystallises in thin needles melting at 39° . *Ethylcatechol carbonate*, $\text{CO}\cdot\text{O}_2\cdot\text{C}_6\text{H}_4\text{Et}$, obtained by the action of water and calcium carbonate on the foregoing *dichloro*-derivative, is a colourless, mobile liquid boiling at $135\text{--}137^\circ$ under 12 mm. pressure.

isoPropylcatechol, $\text{CHMe}_2\cdot\text{C}_6\text{H}_3(\text{OH})_2$, prepared by distilling *isopropyl*-veratrole (compare Behal and Tiffeneau, *Bull. Soc. chim.*, 1903, 29, 1108) with a solution of hydriodic acid, boils at $167\text{--}169^\circ$ under 26 mm., or at $270\text{--}272^\circ$ under the ordinary pressure, crystallises from light petroleum ($30\text{--}60^\circ$) in plates melting at 78° , and is also prepared similarly to the preceding compound by treating *isopropylcatechol* methylene ether (*loc. cit.*) with phosphorus pentachloride, whereby it is converted into *isopropylcatechol dichloromethylene ether*,

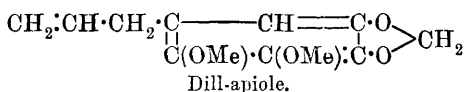
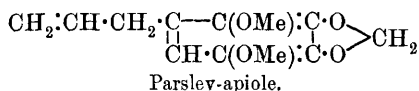


boiling at $131\text{--}134^\circ$ under 12 mm. pressure, and decomposed by boiling with water, forming *isopropylcatechol*.

isoPropylcatechol carbonate, $\text{CHMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}_2\cdot\text{CO}$, prepared similarly to the corresponding ethyl compound, boils at $135\text{--}137^\circ$ under 13 mm

pressure and crystallises in leafy needles melting at 41° , readily soluble in the ordinary organic solvents. M. A. W.

Constitution of Parsley-apiole and Dill-apiole. HERMANN THOMS (*Arch. Pharm.*, 1904, 242, 344—347).—Parsley-apiole has been shown to be 2:5-dimethoxy-3:4-methyleneoxy-1-allylbenzene (*Ber.*, 1903, 36, 1714). In a similar manner, dill-apiole has now been shown to be 5:6-dimethoxy-3:4-methyleneoxy-1-allylbenzene:



C. F. B.

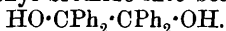
Some Phenolic Ethers containing the pseudo-Allyl Chain, R·CMe:CH₂. AUGUSTE BÉHAL and MARC TIFFENEAU (*Compt. rend.*, 1904, 139, 139—141).—By the action of magnesium methiodide on cyclic alkyl esters, tertiary alcohols of the type CRMe₂·OH can be prepared; *m*-methoxyphenyldimethylcarbinol, OMe·C₆H₄·CMe₂·OH, melts at 34° , and veratryldimethylcarbinol, C₆H₃(OMe)₂·CMe₂·OH, melts at 78° . In addition to the tertiary alcohol, the pseudo-propenyl derivative, R·CMe:CH₂, is also formed, and in the presence of excess of magnesium methiodide forms the sole product (compare Abstr., 1901, i, 246, 272), and the following ψ -allyl derivatives of phenolic ethers have been thus prepared: *o*- ψ -propenylanisole boils at 198 — 199° , has a sp. gr. 0.983 at 21° , and n_D 1.5315; *m*- ψ -propenylanisole boils at 215 — 216° , has a sp. gr. 1.009 at 0° , and n_D 1.5417; 1- ψ -propenyl-3:4-guaiacol boils at 257 — 258° , has a sp. gr. 1.0832 at 15° , and n_D 1.5595; 1- ψ -propenyl-3:4-veratrole boils at 253 — 254° , has a sp. gr. 1.051 at 15° , and n_D 1.5560; 1- ψ -propenyl-3:4-catechol methylene ether boils at 238 — 239° , has a sp. gr. 1.124 at 15° , and n_D 1.5619. The physical properties of the pseudo-propenyl derivatives of the phenolic ethers are intermediate between those of the corresponding propenyl and isopropenyl derivatives. M. A. W.

Syntheses by means of Sodium Phenyl and of Magnesium Alkyl Bromides. SALOMON F. ACREE (*Ber.*, 1904, 37, 2753—2764).—The syntheses previously effected by means of sodium phenyl (bromobenzene and sodium) can be more advantageously carried out by using magnesium phenyl bromide, and a number of syntheses of this kind are described, including that of triphenylcarbinol from benzophenone and magnesium phenyl bromide, and diphenyl α -naphthylcarbinol, C₁₀H₇·CPh₂·OH, from benzophenone and magnesium α -naphthyl bromide, or from phenyl- α -naphthylketone and magnesium phenyl bromide, and of phenyl- α -naphthylcarbinol, C₁₀H₇·CHPh·OH, from benzaldehyde and magnesium α -naphthyl bromide.

as-*Phenyl- α -naphthylethylene*, $C_{10}H_7 \cdot CPh \cdot CH_2$, prepared by the action of magnesium methyl iodide on phenyl α -naphthyl ketone, boils at $350-355^\circ$, crystallises from alcohol, and melts at 60° . The *bromo-derivative*, $C_{10}H_7 \cdot CPh \cdot CHBr$, prepared by the direct action of bromine on the hydrocarbon dissolved in chloroform, is an oil which distils at $240-260^\circ$ under 15 mm. pressure.

When sodium is allowed to act on magnesium phenyl bromide, the products are diphenyl and triphenylcarbinol.

Phenylbenzoin, $OH \cdot CPh_2 \cdot CPh$, is formed by the action of magnesium phenyl bromide on benzil, and is converted by the further action of magnesium phenyl bromide into benzopinacone,

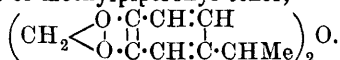


α -Naphthylbenzoin, $C_{10}H_7 \cdot CPh(OH) \cdot CPh$, prepared by the action of magnesium α -naphthyl bromide on benzil, crystallises from alcohol and melts at $132-133^\circ$.

When magnesium phenyl bromide is allowed to act on methyl benzilate, the product is benzopinacone. *s-Diphenyldi- p -tolylpinacone*, $C_6H_4Me \cdot CPh(OH) \cdot CPh(OH) \cdot C_6H_4Me$, prepared by a similar method, crystallises from alcohol and melts at $163-164^\circ$.

Triphenylethylene glycol, $HO \cdot CPh_2 \cdot CHPh \cdot OH$, can be prepared by the action of magnesium phenyl bromide on benzoin or on methyl mandelate. *Diphenyl- p -tolylglycol*, $C_6H_4Me \cdot CPh(OH) \cdot CHPh \cdot OH$, prepared by the action of magnesium p -tolyl bromide on benzoin, crystallises from alcohol and melts at 168° . *Diphenyl- α -naphthylglycol* crystallises from alcohol and melts at 198° .
T. M. L.

Methylpiperonyl Ether. EFISIO MAMELI (*Atti R. Accad. Lincei*, 1904, [v], 13, i, 717-723. Compare this vol., i, 668).—The substance melting at 111° (*loc. cit.*) obtained by the interaction of piperonaldehyde and magnesium methyl iodide is now found to be more readily prepared by the etherification of methylpiperonyl alcohol by inorganic salts, and to consist of methylpiperonyl ether,



It crystallises from alcohol or benzene in shining, rectangular prisms united in groups often 2 cm. long and 5 mm. broad; it is soluble in chloroform and to a lesser extent in ether or acetic acid. It does not decolorise a chloroform solution of bromine, combine with phenylhydrazine, hydroxylamine, or benzoyl chloride, or reduce ammoniacal silver nitrate solution, but it reduces Fehling's solution slightly. With cold sulphuric acid, it yields a bright red solution which gradually deposits violet flocks. With concentrated nitric acid, even at 0° , it gives a mixture of various nitro-derivatives. On heating, it first yields methylenedioxy-styrene and methylpiperonyl alcohol: $(CH_2 : O_2 : C_6H_3 \cdot CHMe)_2 O = CH_2 : O_2 : C_6H_3 \cdot CH : CH_2 +$

$CH_2 : O_2 : C_6H_3 \cdot CHMe \cdot OH$;
the latter then decomposes, giving another molecule of methylenedioxy-styrene: $CH_2 : O_2 : C_6H_3 \cdot CHMe \cdot OH = H_2O + CH_2 : O_2 : C_6H_3 \cdot CH : CH_2$.

By a few salts of the heavy metals at the ordinary temperature and at 100° by most of them or by salts of the alkali or alkaline-earth metals, methylpiperonyl alcohol is converted into methylenedioxy

styrene, a change also brought about by the action of heat; at the ordinary temperature, it is transformed into methylpiperonyl ether if it is contaminated with traces of salts of the alkali or alkaline-earth metals remaining after its extraction. T. H. P.

Diethylantranilic Acid. HANS MEYER (*Monatsh.*, 1904, 25, 487—490. Compare Abstr., 1901, i, 190; Willstätter and Kahn, this vol., i, 235).—The action of ethyl iodide on anthranilic acid leads to the formation of *diethylantranilic acid*, $\text{NEt}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, which separates from acetic anhydride in glistening crystals, melts at 120 — 121° , and is neutral to potassium hydroxide and phenolphthalein. The *hydriodide* melts and decomposes at 160° ; the *periodide* forms dark violet crystals; the hydrochloride melts and decomposes at 172° . The hydrochloride and the iodide are decomposed by silver oxide; with potassium hydroxide, they form *potassium* salts, for instance, $\text{CO}_2\text{K} \cdot \text{C}_6\text{H}_4 \cdot \text{NHEt}_2\text{I}$. The successive action of thionyl chloride and alcohol on the acid leads to the formation of the *hydrochloride* of the ester, from which the ester is liberated by dilute sodium carbonate solution. G. Y.

Condensation of Aldehydes and Lactones with Dibasic Acids. RUDOLPH FITTIG (*Annalen*, 1904, 331, 151—196; Abstr., 1890, 583).—I. *Condensation of Cinnamaldehyde with Succinic Acid.*—[With LUDWIG BATT.]—In continuation of earlier investigations (*loc. cit.*) the behaviour of cinnamaldehyde towards sodium succinate in the presence of acetic anhydride has been studied. Paraconic acid was not produced, but cinnamerylisocrotonic acid, the sodium salt of which condenses at the same time with 2 mols. of cinnamaldehyde, water and carbon dioxide being eliminated, forming the hydrocarbon, *αβ-diphenyldibutadiene*, $\text{CHPh}:\text{CH}:\text{CH}:\text{CH}:\text{CH}:\text{CH}:\text{CH}:\text{CHPh}$. At a higher temperature, the anhydride of dicinnamylidenesuccinic acid, $\text{CHPh}:\text{CH}:\text{CH}:\text{CH}:\text{C}(\text{CO})\text{CO}$, together with a small amount of the unsaturated acid, is formed.

Molecular proportions of cinnamaldehyde, acetic anhydride, and dry sodium succinate are heated together for 20 hours at 90° ; the product is treated with aqueous sodium carbonate and the mixture extracted with ether, when diphenyldibutadiene separates between the aqueous and ethereal layers; it crystallises in golden-yellow leaflets from acetic acid, melting and decomposing at 225° . When brominated in suspension in chloroform, a crystalline *tetrabromide*, which melts and decomposes at 185° , and an insoluble crystalline *octobromide*, melting and decomposing at 248° , are obtained. *Cinnamerylisocrotonic acid*, $\text{CHPh}:\text{CH}:\text{CH}:\text{CH}:\text{CH}_2\text{CO}_2\text{H}$, is contained in the alkaline aqueous extract of the reaction product, and is separated from the cinnamic acid by fractional crystallisation of their calcium salts; it crystallises in leaflets melting at 111 — 112° ; the *silver* salt is a curdy precipitate, and the *calcium* and *barium* salts crystallise with $2\text{H}_2\text{O}$. On reduction with sodium amalgam, *hydrocinnamerylisocrotonic acid*,

$\text{CH}_2\text{Ph}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, is formed and crystallises in needles melting at 88° ; the *silver* salt is a white precipitate, and the *barium* salt crystallises with $2\text{H}_2\text{O}$. This acid yields a *dibromide* which forms crystals melting and decomposing at $103\text{--}104^\circ$.

When the mixture above mentioned is heated for the same time at 130° and then treated with aqueous alkali, the *anhydride* of di-cinnamylidenesuccinic acid separates between the aqueous and ethereal layers; it crystallises in red needles or leaflets melting and decomposing at 215° . It is converted into the *acid* by heating with aqueous sodium hydroxide; the latter is a white, amorphous powder, which, on suddenly heating or on warming with acetic anhydride, is converted into the red anhydride. The *silver* salt is a yellow precipitate, and the *calcium* and *barium* salts are yellow powders crystallising with $4\text{H}_2\text{O}$. On reduction, *hydrodicinnamylidenesuccinic acid*, $\text{C}_8\text{H}_6\text{Ph}_2(\text{CO}_2\text{H})_2$, is obtained, crystallising in needles melting at 182° ; the *silver* salt is a white precipitate, and the *barium* salt is a crystalline powder. The *tetrabromide* crystallises in needles melting at 201° . When heated a few degrees above its melting point, hydrocinnamylidenesuccinic acid is converted into its *anhydride*, which crystallises in needles melting at 164° .

II. *Condensation of Benzaldehyde with Itaconic Acid*.—[With KARL BOCK.]—Benzaldehyde and sodium itaconate either do not react in the presence of acetic anhydride, or form a tarry mass; when the condensation is effected by Claisen's method, two stereoisomeric

dilactones, $\begin{array}{c} \text{O} \text{---} \text{CO} \text{---} \text{CH} \text{---} \text{CHPh} \\ | \qquad \qquad | \\ \text{CHPh} \cdot \text{CH} \cdot \text{C} \cdot \text{CO} \cdot \text{O} \end{array}$, are formed; they are probably produced by the condensation of benzaldehyde with a lactonic acid, $\begin{array}{c} \text{CH}_2 \cdot \text{C} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CHPh} \\ | \\ \text{CO} \text{---} \text{O} \end{array}$

A mixture of ethyl itaconate (1 mol.) and benzaldehyde (2 mols.) is slowly added to a suspension of sodium ethoxide in ether, and the mixture kept for 2 days, when it is treated with ice-water and an aqueous solution of alkali, and then extracted with ether to remove by-products; after acidification, a mixture of the two lactones separates, from which *isodiphenylheptenedilactone* is obtained, by treatment with ether, as a white solid, crystallising in needles melting at 234° and less soluble than the isomeride. The *diphenylheptenedilactone*, $\text{C}_{19}\text{H}_{14}\text{O}_4$, is soluble in the ether, from which it separates in needles (m. p. 161°); it is very readily converted into *hydroxydiphenylheptenelactonic acid*, the *barium* salt of which, $(\text{C}_{19}\text{H}_{15}\text{O}_5)_2\text{Ba}\cdot\text{H}_2\text{O}$, forms prismatic plates and the *silver* salt a crystalline powder. The *dibasic dihydroxy-acid* forms crystalline *barium*, $\text{C}_{19}\text{H}_{16}\text{O}_6\text{Ba}$, and *calcium* salts, and an amorphous, insoluble *silver* salt. Neither the hydroxylactonic nor the dihydroxy-acid could be prepared. The *isodilactone* forms crystalline *barium* and *calcium* salts and an amorphous *silver* salt, and can be quantitatively converted into the isomeride by boiling with bases; the reverse change could not be effected. All attempts to decompose the dilactones into benzaldehyde and the lactonic acid above mentioned were unsuccessful.

When treated with bromine in suspension in chloroform, both

dilactones yield a *diphenyldibromoheptodilactone*, $C_{19}H_{14}O_4Br_2$, which crystallises in colourless leaflets melting at 192° , and with hydrobromic acid in acetic acid solution a *diphenylbromoheptodilactone*, $C_{19}H_{15}O_4Br$, crystallising in colourless needles melting at 186° . When treated with dilute sodium hydroxide, both bromo-compounds dissolve, and on acidification yield diphenylheptenedilactone (m. p. 161°).

On reducing either of the lactones in alkaline solution with sodium amalgam, or by similar treatment of the bromo-compounds, *diphenylheptodilactone*, $C_{19}H_{16}O_4$, is formed, crystallising in needles melting at 149° , and decomposing at 157° . When treated with cold aqueous alkali, only one lactone ring is broken, salts of the monobasic hydroxy-acid being obtained; the *barium* salt, $(C_{19}H_{17}O_5)_2Ba$, and the *silver* salt both being crystalline. The corresponding dihydroxy-dibasic acid forms sparingly soluble *barium*, $(C_{19}H_{18}O_6)Ba$, *calcium*, and *silver* salts. Neither of the acids could be isolated.

III. *Condensation of Valerolactone with Succinic Acid*.—[With HARRY SALOMON and GEORG WERNHER.]—When ethyl succinate and valerolactone are heated with sodium ethoxide and the product treated with aqueous alkali, extracted with chloroform to remove neutral substances, acidified with hydrochloric acid, and again extracted with chloroform, an oil is obtained; on boiling this oil with water and removing from the aqueous liquor by ether any material soluble in that solvent,

valactenesuccinic anhydride, $\begin{array}{c} CH_2-CH_2-CH_2\cdot CO \\ | \quad \quad | \quad \quad | \\ CHMe\cdot O\cdot C=C-C-CO \end{array} > O$, remains in aqueous solution; it crystallises in needles melting at 182° . When treated with bases, the salts of valactenesuccinic acid (which has not been isolated) are obtained; the *barium* and *calcium* salts are crystalline and the *silver* salt amorphous.

The ethereal extract mentioned above contains a neutral substance melting at 155° . The alkaline extract of the original oil contains an acid which can be purified by distillation under reduced pressure; *valactenepropionic acid*, $\begin{array}{c} CH_2\cdot CH_2 \\ | \quad \quad | \\ CHMe\cdot O \end{array} > C:CH\cdot CH_2\cdot CO_2H$, is a colourless, mobile liquid boiling at $143.5-144^\circ$ under 30 mm. pressure, and boiling and decomposing at $253-255^\circ$ under 60 mm. pressure. The *barium*, *calcium*, and *silver* salts are amorphous and unstable.

K. J. P. O.

Isomeric Esters of o-Aldehydo-acids. HANS MEYER (*Monatsh.*, 1904, 25, 491-499).—The successive action of thionyl chloride and methyl alcohol on mucobromic acid leads to the formation of a mixture of the *n-ester*, which is an oil and boils at $230-234^\circ$, and the *ψ-ester*, which is a hard, white, crystalline substance and boils at $249-251^\circ$ (Simonis, Abstr., 1901, i, 268).

When acted upon by thionyl chloride and the product treated with methyl or ethyl alcohol, aldehydophthalic acid yields the normal esters.

Methyl aldehydophthalate, $COH\cdot C_6H_4\cdot CO_2Me$, is a colourless oil, which boils at $220-222^\circ$. It is also obtained when the acid is boiled with methyl alcohol and sulphuric acid. The *ψ-methyl ester*, which is

formed when the acid is boiled with methyl alcohol, boils at 242—245°.

Ethyl aldehydophthalate is a colourless oil, which boils with slight decomposition at 240—243°. When boiled with ethyl alcohol and sulphuric acid, aldehydophthalic acid forms the ψ -ester.

These normal esters of aldehydophthalic acid were previously obtained, but not purified, by Stabil (see Wegscheider, Dúbrav, and Rušnov, this vol., i, 59).

In the action of thionyl chloride on aldehydophthalic acid, Stabil's anhydride melting at 202—210° is obtained as a by-product.

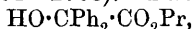
G. Y.

***o*-Benzoylbenzoic Acid.** HANS MEYER (*Monatsh.*, 1904, 25, 475—486. Compare Haller and Guyot, *Abstr.*, 1900, i, 170; 1901, i, 146).—If *o*-benzoylbenzoic acid is converted into its chloride by the action of thionyl chloride at 30—35° or of phosphorus pentachloride at 40°, the excess of reagent rapidly evaporated off under reduced pressure, and the product treated immediately with methyl alcohol, the *methyl* ester obtained crystallises in monoclinic prisms, melts at 80—81°, boils at 345—348°, and is easily soluble in alcohol, ether, acetone, or chloroform, and dissolves in sulphuric acid to a lemon-yellow solution. The action of methyl sulphate on sodium *o*-benzoylbenzoate, of methyl alcohol and concentrated sulphuric acid on the acid, or of methyl iodide on the dry silver salt leads to the formation of the methyl ester, which melts at 52° and boils at 350—352°. It dissolves in concentrated sulphuric acid to a colourless solution, which becomes yellow after some hours.

The author discusses the constitution of the isomeric methyl esters.

G. Y.

Esterification of Benzilic and Mandelic Acids. SALOMON F. ACREE (*Ber.*, 1904, 37, 2764—2768).—*n*-Propyl benzilate,

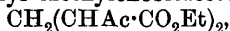


boils at about 220° under 35 mm. pressure. *iso*Amyl benzilate boils at 230—232° under 26 mm. pressure.

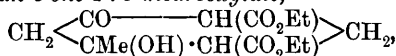
T. M. L.

1:5-Diketones. II. PAUL RABE (*Annalen*, 1904, 332, 1—21. Compare *Abstr.*, 1902, i, 709).—Knoevenagel's views (*Abstr.*, 1903, i, 636) as to the impossibility of distinguishing between the 1:5-diketones, the *cyclohexendiones*, and the cyclic ketonic alcohols, *cyclohexanolones*, are criticised. After a discussion of the facts which are known at present, it is concluded that these two classes of compounds, although nearly related, can be sharply distinguished by the following reactions: (i) they behave differently towards such reagents as sodium ethoxide, ammonia, and substituted ammonias, (ii) in many cases, two structural (but desmotropic) isomerides have been isolated, (iii) the condensation processes in which they are formed can be shown to consist of two phases, namely, the formation of the 1:5-diketone and the transformation of this compound into the cyclic compound under the influence of such bases as piperidine; the base is not necessary to the preliminary condensation, but only to the subsequent isomeric change. Thus, formaldehyde and ethyl acetoacetate in

the absence of any base (compare Knoevenagel, Abstr., 1895, i, 48) condense to form ethyl methylenebisacetoacetate,

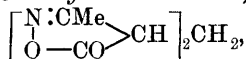


an oil, which, in the presence of piperidine, passes into *ethyl 4-hydroxy-4-methylcyclohexan-6-one-1:3-dicarboxylate*,



a solid, which can be converted by way of the sodium salt into the liquid dienolic form, $\text{CH}_2 \left\langle \begin{array}{c} \text{C}(\text{OH}) \text{---} \text{C}(\text{CO}_2\text{Et}) \\ \text{CMe}(\text{OH}) \cdot \text{CH}(\text{CO}_2\text{Et}) \end{array} \right\rangle \text{CH}_2$, which slowly changes, on keeping, into the solid keto-enolic form.

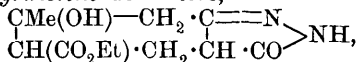
Condensation Products from Ethyl Acetoacetate and Formaldehyde.—[With F. RAHM.]—When ethyl acetoacetate (2 mols.) and formaldehyde (1 mol.) are brought together in aqueous alcoholic solution, a very pure specimen of ethyl methylenebisacetoacetate is obtained, but the best yield is found when a large excess of the aldehyde is used. The product thus obtained boils at 215—218° under 35—37 mm. pressure, and gives a wine-red coloration with an alcoholic solution of ferric chloride. On treating the ester (1 mol.) in aqueous alcoholic solution at the ordinary temperature with hydroxylamine hydrochloride (2 mols.), *4-methylenebis-3-methyl-5-isooxazolone*,



separates in colourless needles melting and decomposing at 180—183°; it has an acid reaction and is soluble in alkalis, but only with difficulty in acids.

The ester of the cyclic ketone-alcohol, *ethyl 4-hydroxy-4-methylcyclohexan-6-one-1:3-dicarboxylate*, is most readily prepared by adding piperidine directly to a mixture of paraformaldehyde and ethyl acetoacetate, cooling, and at the same time removing water by the addition of anhydrous sodium sulphate; the ester crystallises in prismatic needles melting indefinitely at 79°; in alcoholic solution, a partial change into the enolic form rapidly takes place. The *sodium* salt, $\text{C}_{13}\text{H}_{19}\text{O}_6\text{Na}$, prepared by the action of sodium on an ethereal solution of the solid ester, is a yellow, hygroscopic powder, from which, by treatment with ice-cold sulphuric acid and ether, the liquid ester of the dienolic form can be obtained; it is a yellow, very viscous oil, giving in alcoholic solution an intense violet reaction and changing gradually into the solid keto-enolic form.

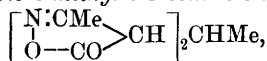
Ethyl hydroxymethylcyclohexanonedicarboxylate and hydrazine hydrate yield a *pyrazolone* derivative,



whether the keto-enolic or the dienolic ester is used; it forms prismatic crystals with a double melting point, 188° and 203°, and is soluble both in acids and alkalis. Ammonia gives, with both the esters, *ethyl 6-imino-4-hydroxy-4-methylcyclohexane-1:3-dicarboxylate*,

$\text{CH}_2 \left\langle \begin{array}{c} \text{C}(\text{NH}) \text{---} \text{CH}(\text{CO}_2\text{Et}) \\ \text{CMe}(\text{OH}) \cdot \text{CH}(\text{CO}_2\text{Et}) \end{array} \right\rangle \text{CH}_2$, which separates in white needles melting at 92°.

Ethyl Ethylidenebisacetoacetate and Methylenebisacetylacetone.—[With F. ELZE.]—Whilst the true 1:5-diketones behave towards ammonia and its derivatives in the normal manner, the condensation product of acetaldehyde and ethyl acetoacetate, which contains ethyl ethylidenebisacetoacetate, gives, with hydroxylamine hydrochloride, a bisisooxazolone, and, with ammonia, ethyl dihydrocollidinedicarboxylate. When the crude oily ethyl ethylidenebisacetoacetate is kept in solution in alcoholic ammonia for several days and the solvent then evaporated, ethyl imino-hydroxydimethylcyclohexanedicarboxylate and ethyl dihydrocollidinedicarboxylate (m. p. 131°) are formed. From a solution containing the same crude ester and hydroxylamine hydrochloride, 4-ethylidenebis-3-methyl-5-isooxazolone,



separates in prismatic needles melting and decomposing at 157° and readily soluble in alkalis and acids.

When acetylacetone and formaldehyde condense in aqueous solution, besides the oily methylenebisacetylacetone, a solid compound, $\text{C}_{11}\text{H}_{16}\text{O}_4$, melting at 79°, and a compound, $\text{C}_{17}\text{H}_{24}\text{O}_6$, melting at 181°, are formed. Methylenebisacetylacetone and hydroxylamine hydrochloride give 4-methylenebis-3:5-dimethylisooxazole, melting at 141–142° (compare Knoevenagel, Abstr., 1903, i, 637).

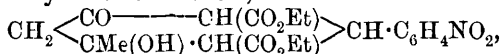
K. J. P. O.

Explanation of Tautomeric Phenomena. II. Desmotropic-isomeric Cyclic β -Ketonic Esters. PAUL RABE and ADOLF BILLMANN (*Annalen*, 1904, 332, 22–37. Compare preceding abstract, and Abstr., 1901, i, 33).—As a continuation of earlier investigations of tautomeric phenomena (*loc. cit.*), it has been ascertained that the desmotropic-isomeric forms of ethyl 4-hydroxy-2:4-dimethylcyclohexane-6-one-1:3-dicarboxylate, ethyl 4-hydroxy-2-*p*-nitrophenyl-4-methylcyclohexane-6-one-1:3-dicarboxylate, and of ethyl 4-hydroxy-2-*m*-nitrophenyl-4-methylcyclohexane-6-one-1:3-dicarboxylate pass readily, one into the other. The molten ketonic or enolic forms or the solutions of these forms always undergo change, a mixture of the two forms resulting. In some cases, when the ketonic form is insoluble and has a high melting point, this form separates in the solid state from such liquid mixtures or from the solutions. Besides existing in ketonic and enolic forms, the 5-*p*-nitrophenyl ester is found in two stereoisomeric modifications, a phenomenon not hitherto observed in cyclic β -ketonic esters.

The keto-form of ethyl 4-hydroxy-2:4-dimethylcyclohexane-6-one-1:3-dicarboxylate, $\text{CH}_2 \left\langle \begin{array}{c} \text{CO} \text{---} \text{CH}(\text{CO}_2\text{Et}) \\ \text{CMe}(\text{OH}) \cdot \text{CH}(\text{CO}_2\text{Et}) \end{array} \right\rangle \text{CHMe}$ (the “ β -ester”), has already been described by Knoevenagel (Abstr., 1895, i, 48); it melts at 80°, gives no coloration with ferric chloride, and slowly decomposes into a viscous oil. The sodium salt of the enolic ester (the “ α -ester”), $\text{C}_{14}\text{H}_{21}\text{O}_6\text{Na}, \text{EtOH}$, is prepared by adding sodium (1 atom) to a solution in absolute alcohol of the keto-ester (1 mol.); it forms white, hygroscopic crystals melting at 75–78°, and decomposes on keeping. The enolic ester (Abstr., 1899, i, 289) prepared from the

sodium salt melts at 60—63° and immediately begins to change into the keto-form.

Whilst Knoevenagel and Hoffmann (Abstr., 1899, i, 116, 214) obtained from ethyl acetoacetate and *p*-nitrobenzaldehyde one ester (m. p. 170—171°), "ethyl *p*-nitrobenzylidenebisacetoacetate," two stereoisomeric cyclic *ketonic esters*,



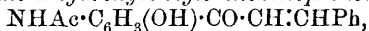
the β_1 - and β_2 -esters, have now been isolated by fractional crystallisation from alcohol; the β_1 -ester crystallises in needles melting at 164° and is doubtlessly identical with Knoevenagel's compound (m. p. 171°); it yields the sodium salt of the α_1 -ester, $\text{C}_{19}\text{H}_{22}\text{O}_8\text{NNa}$, which melts at 152° and is hydrolytically dissociated in water, part of the ester changing into the β_1 -ester, which then crystallises out. The α_1 -ester is prepared from the sodium salt by treatment with dilute sulphuric acid and ice, and crystallises in rhombic leaflets melting at 129—130°; it is very stable, has a marked acid character, and gives with ferric chloride an intense violet coloration, but partially changes into the β_1 -form when molten; it is more soluble than the β_1 -form.

The β_2 -ester, which is more soluble than the β_1 -ester, crystallises in rhombic leaflets melting at 152—153°, and can be converted into the corresponding enolic form, the α_2 -ester, by way of the sodium salt; this enolic form forms prismatic crystals, melting at 130—135°, when it partially passes into the keto-form. In the molten state or in solution these four isomeric esters are unstable and in time yield an allelo-tropic mixture.

The β -ester, the ketonic form, of ethyl 4-hydroxy-2-*m*-nitrophenyl-4-methylcyclohexane-6-one-dicarboxylate was prepared according to Knoevenagel's method (*loc. cit.*) and crystallises in slender, prismatic needles melting at 146°, when it partly changes into the enolic form. The sodium salt of the enolic form, the α -ester, $\text{C}_{19}\text{H}_{22}\text{O}_8\text{NNa} \cdot \text{EtOH}$, prepared in the usual way, forms lemon-yellow, hygroscopic crystals melting at 151°. The α -ester is obtained from the β -ester by dissolving the latter in alcohol, adding a concentrated solution of sodium ethoxide in alcohol, and then pouring into ice-cold dilute sulphuric acid; the α -ester forms a yellow oil, which very rapidly changes into the β -form; in alcoholic solution, it gives a violet coloration with ferric chloride.

K. J. P. O.

5-Acetylamino-2-hydroxybenzylideneacetophenone. FRANZ KUNCKELL (*Ber.*, 1904, 37, 2826—2827. Compare Abstr., 1903, i, 509).—5-Acetylamino-2-hydroxybenzylideneacetophenone,

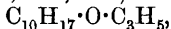


is formed when 5-acetylamino-2-hydroxyacetophenone is heated with benzaldehyde in alcoholic sodium hydroxide solution and the product treated with hydrochloric acid. It crystallises in yellow needles, melts at 190°, is easily soluble in aqueous alkali hydroxides or alcohol, and, when heated with acetic anhydride and sodium acetate, yields the triacetyl compound, $\text{NAc}_2 \cdot \text{C}_6\text{H}_3(\text{OAc}) \cdot \text{CO} \cdot \text{CH} : \text{CHPh}$, which forms long, white needles and melts at 147°. With bromine in carbon disulphide

solution, the triacetyl compound forms a *dibromide* which melts at 170°. G. Y.

Stereoisomeric Oximes of Dypnone (Diphenyl-1-methylpropenon-3). FERDINAND HENRICH and A. WIRTH (*Monatsh.*, 1904, 25, 423—442. Compare this vol., i, 431).—When treated with acetic anhydride and a drop of sulphuric acid, *syn*-dypnoneoxime yields an *acetyl* derivative which crystallises in stellate groups of needles, melts at 74°, is easily soluble in alcohol or ether, and is hydrolysed to the *syn*-oxime by alcoholic potassium hydroxide. With phenylcarbimide, the *syn*-oxime forms a *derivative* which separates from benzene in white crystals and melts at 149—150°. Reduction of the *syn*-oxime with sodium and amyl alcohol leads to the formation of $\alpha\beta$ -diphenyl- β -methylallylamine hydrochloride, $\text{CMePh}\cdot\text{CH}\cdot\text{CHPh}\cdot\text{NH}_2\cdot\text{HCl}$; the *platinichloride* is yellow, crystallises from alcohol, and melts at 198°; the *picrate* forms yellow crystals and melts at 191°. G. Y.

Influence of the Introduction of Unsaturated Radicles on the Rotatory Power of Certain Molecules. Allyl Ethers of Borneol, Menthol, β -Methylcyclohexanol, and of Linalool. ALBIN HALLER and FRANÇOIS MARCH (*Compt. rend.*, 1904, 138, 1665—1669. Compare Abstr., 1903, i, 503, 563, 628).—*Bornyl allyl ether*,



obtained by the action of allyl iodide on the sodium derivative of borneol, is a liquid boiling at 105—107° under 17 mm. pressure, has a sp. gr. 0.9376 at 0°/4°, or 0.9221 at 21°/4°, molecular refraction = 59.15, theoretical value 59.025, and $[\alpha]_D - 59^\circ 6'$, the rotatory power of the borneol used being $[\alpha]_D - 35^\circ 40'$. *Menthyl allyl ether*, $\text{C}_{10}\text{H}_9\cdot\text{O}\cdot\text{C}_3\text{H}_5$, prepared similarly to the preceding compound, is a colourless liquid with a characteristic odour, boiling at 103—104° under 13 mm. pressure, has a sp. gr. 0.8830 at 0°/4°, or 0.8763 at 19°/4°, molecular refraction 61.01, theoretical value 61.127, $[\alpha]_D - 98^\circ 30'$, whilst the menthol employed had $[\alpha]_D - 49^\circ 4'$. *β -Methylcyclohexyl allyl ether*, $\text{C}_7\text{H}_{13}\cdot\text{O}\cdot\text{C}_3\text{H}_5$, obtained by heating the sodium derivative of β -methylcyclohexanol prepared by Kondakoff and Schindelmeiser's method (*J. pr. Chem.*, 1900, [ii], 61, 482) with allyl bromide, boils at 79—81° under 18 mm. pressure, has a sp. gr. 0.8837 at 0°/4°, or 0.8738 at 15°/4°, molecular refraction 47.58, the theoretical value being 47.31, and $[\alpha]_D - 14^\circ 20'$. The β -methylcyclohexanol employed had $[\alpha]_D + 1^\circ 30'$ and was not quite free from β -methylcyclohexanone. *Linalyl allyl ether*, $\text{C}_{10}\text{H}_{17}\cdot\text{O}\cdot\text{C}_3\text{H}_5$, prepared similarly to the isomeric bornyl compound, is a colourless liquid boiling at 103—105° under 15 mm. pressure, has a sp. gr. 0.8722 at 0°/4°, or 0.8665 at 16°/4°, molecular refraction 61.45, the theoretical value being 62.43, $[\alpha]_D + 2^\circ 2'$, whilst the linalool employed had $[\alpha]_D - 6^\circ 20'$.

With the exception of linalyl allyl ether, the allyl ethers of the alcohols examined have a higher specific rotation than the original alcohol.

Attempts to prepare the propyl ethers of the same alcohols by the action of propyl iodide on the sodium derivative of the alcohol were unsuccessful (compare Abstr., 1903, i, 503, and Hecht, Conrad, and

Brückner, Abstr., 1890, i, 4). By the action of propyl *p*-toluenesulphonate on the sodium derivative of menthol, two liquids were obtained, one, probably propyl menthyl ether, boiling at 112—114° under 19 mm. pressure, having $[\alpha]_D -43^\circ 40'$, the other boiling at 114—116° under 19 mm. pressure.

M. A. W.

Terpenes and Ethereal Oils. Camphorophorone and its Decomposition. OTTO WALLACH [with FRITZ COLLMANN] (*Annalen*, 1904, 331, 318—333).—Although dihydropulegenone and dihydrocamphorophorone have been shown to be identical (Abstr., 1903, i, 567), the corresponding unsaturated ketones, $C_9H_{14}O$, pulegenone and camphorophorone, are isomeric, their relation being expressed by the formulæ $\begin{array}{c} CHMe \cdot CO \\ | \\ CH_2 - CH \end{array} > CPr^\beta$ and $\begin{array}{c} CHMe \cdot CO \\ | \\ CH_2 - CH_2 \end{array} > C: CMe_2$. The ready decomposition of pulegenone by acids into acetone and 1:2-methylcyclopentanone is not found to occur under the same conditions in the case of camphorophorone, which is only decomposed by alkaline reagents.

The yield of camphorophorone reaches a maximum of 44 per cent. when calcium camphorate, completely dried, is distilled; if the calcium salt is distilled with soda-lime, the yield falls to 24 per cent., and if the soda-lime is moist, the yield falls to 13 per cent., an increasing quantity of 1:2-methylcyclopentanone appearing in the distillate. The latter can be recognised and isolated as *semicarbazone*, which melts at 174—176°; 1:2-methylcyclopentanone is an oil boiling at 140—141°, which has a sp. gr. 0.917 and $n_D 1.4348$ at 20°; the *oxime* is a liquid boiling at 100—102° under 18 mm. pressure. When oxidised with chromic and sulphuric acids or with neutral potassium permanganate, the pentanone is easily converted into γ -acetylbutyric acid, the *semicarbazone* of which melts at 170—171°, these facts demonstrating the constitution of the pentanone.

That the methylcyclopentanone is actually formed from the camphorophorone is shown by the fact that it is produced in large quantities together with acetone when camphorophorone is dropped on molten potassium hydroxide.

Pure camphorophorone reacts more rapidly with semicarbazide acetate than does the crude material; the normal *semicarbazone* melts at 197° and readily combines with another mol. of semicarbazide, forming a *semicarbazide-semicarbazone*, which melts at 135° and is produced when camphorophorone is treated with excess of semicarbazide in acetic acid solution; it combines with picric acid forming a yellow, crystalline compound melting at 146—147°. Camphorophorone can only be recovered with difficulty from its semicarbazone by warming with sulphuric acid, and when purified in this manner boils at 199—201°, has a sp. gr. 0.93, and $n_D 1.4897$ at 20°; it shows, therefore, the optical behaviour of an alcohol with two ethylenic linkings, and thus resembles pulegone, *isothujone*, *carvenone*, *menthenone*, &c.

Kerp and Müller (Abstr., 1898, i, 265) found that from the additive product of sulphur dioxide and camphorophorone an isomeric substance, β -camphorophorone, is obtained, to which the formula of pulegenone has been ascribed. On repeating these experiments, it was found that β -camphorophorone is nothing but camphorophorone in a very pure state;

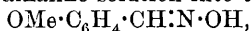
in fact, the formation of the additive product with sulphur dioxide affords the best method of purifying camphorophorone. Pulegone behaves in the same manner towards sulphur dioxide.

The normal *oxime* of camphorophorone is prepared in the same manner as the normal compound of pulegone, and is a viscid oil which distils under reduced pressure and is volatile with steam; it is soluble in dilute acids.

K. J. P. O.

Terpenes and Ethereal Oils. Additive Products of Nitrogen Trioxide and Nitrosyl Chloride with Unsaturated Compounds. OTTO WALLACH (*Annalen*, 1904, 332, 305—336).—After an historical *résumé* of recent work on the additive compounds formed by the action of nitrogen trioxide and peroxide and of nitrosyl chloride on unsaturated compounds, a method of transforming aliphatic α -ketones into β -ketones and *vice versa* is described, thus: $\text{COPhEt} \rightarrow \text{CHPhEt} \cdot \text{OH} \rightarrow \text{CHPh} \cdot \text{CHMe} \rightarrow [\text{CHPh}(\text{NO}) \cdot \text{CHMe}(\text{NO}_2)]_2 \rightarrow \text{CHPh} \cdot \text{CMe} \cdot \text{NO}_2 \rightarrow \text{CH}_2\text{Ph} \cdot \text{CMe} \cdot \text{NOH} \rightarrow \text{CH}_2\text{Ph} \cdot \text{CMe}$ (compare Abstr., 1902, i, 806, and this vol., i, 424).

Compounds of the Anethole Series.—[With HANS MÜLLER.]—Anethole nitrite (compare Wieland, this vol., i, 54) is prepared by adding a concentrated solution of sodium nitrite to a solution of sulphuric acid, on which lies a solution of anethole in petroleum. The β -nitroanethole, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CMe} \cdot \text{NO}_2$, prepared by Tönnies' method (Abstr., 1883, 264) from the nitrite, is easily converted by digestion with hydroxylamine hydrochloride in alkaline solution into the oxime,



which crystallises in prisms melting at 61° ; its *benzoyl* derivative melted at 109° . When the β -nitroanethole is warmed with potassium carbonate alone, anisaldehyde is obtained; on treatment with hydrochloric acid, anisaldehyde and hydroxylamine are produced. On reducing the nitro-compound with zinc dust and acetic acid, an *oxime*. $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CMe} \cdot \text{N} \cdot \text{OH}$, is formed, which melts at 65 — 66° and distils at 160 — 170° ; the *hydrochloride* melts at 123 — 124° . On hydrolysing the oxime with dilute sulphuric acid and distilling the product with steam, the *ketone*, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CMe}$, is obtained as an oil boiling at 141° , and having a sp. gr. 1.07, and $[n]_D$ 1.5253 at 20° ; with hydroxylamine, it yields the oxime from which it was produced, and with semicarbazide a *semicarbazone*, $\text{C}_{11}\text{H}_{15}\text{O}_2\text{N}_3$, which crystallises in leaflets melting at 175° . That the ketone is not identical with the other possible product, methoxyphenyl ethyl ketone, was shown by a comparison of the benzoyl derivatives and the semicarbazones (compare Wallach and Pond, Abstr., 1896, i, 94). Further, when oxidised with sodium hypobromite, bromoform and anisic acid together with anisylacetic acid (m. p. 85 — 86°) are produced.

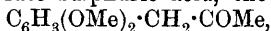
When the stable anethole nitrosochloride is warmed with alcohol, it is converted into anisaldehyde and hydroxylamine hydrochloride. Sodium methoxide in methyl-alcoholic solution acts on the nitrosochloride, producing the *sodium* salt, $\text{C}_{11}\text{H}_{14}\text{O}_3\text{NNa}$ (crystallising in needles), of the *oxime*, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{NOH}) \cdot \text{CHMe} \cdot \text{OMe}$, which is obtained from the sodium salt by the action of carbon dioxide; it melts at 48 — 49° and distils under reduced pressure at 194° . The *hydrochloride*

melts at 125°. When hydrolysed with dilute sulphuric acid at 80°, the *ketone*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CHMe}\cdot\text{OMe}$, is obtained as a yellow oil distilling under reduced pressure at 160°; its *semicarbazone* melts at 192°; on oxidation with chromic acid, it is converted into anisaldehyde and acetic acid together with a little anisic acid.

Compounds of the isoSafrole Series.—[With HANS MÜLLER.]—By warming *isosafrole* nitrite (m. p. 128°) either with acetyl chloride or with sodium methoxide or alcoholic potassium hydroxide, β -*nitroisosafrole*, $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\cdot\text{CH}\cdot\text{CMe}\cdot\text{NO}_2$, is obtained in yellow crystals melting at 98°; when warmed with hydroxylamine hydrochloride and sodium carbonate in alcoholic solution, it is converted into piperonaldoxime (m. p. 111°; compare Angeli, 1893, i, 261). On reduction of the nitro-compound, the *oxime*, $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{NOH}$, which melts at 86–87°, is formed, and is converted by treatment with dilute sulphuric acid into the corresponding *ketone*, boiling at 156° under reduced pressure and having a sp. gr. 1.203 and $[n]_D$ 1.5430 at 20°. The *semicarbazone* melts at 163°. When the *ketone* is oxidised with sodium hypobromite, piperonylic (m. p. 228°) and piperonylacetic acids (m. p. 127–128°) are formed, together with a hydroxy- or ketonic acid.

On treating the nitrosochloride of *isosafrole* with sodium methoxide, an *oxime*, $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\cdot\text{C}(\text{NOH})\cdot\text{CHMe}\cdot\text{OMe}$, is obtained, which melts at 74° and boils under reduced pressure at 200–205°; its *hydrochloride* melts at 98°; the *ketone*, prepared from the *oxime* by the action of dilute sulphuric acid, is a yellow oil, boiling at 173–174° under reduced pressure, which yields a *semicarbazone* melting at 181°.

Compounds of the Methylisoeugenole Series.—[With ERICH BESCHKE.]—The nitrite of methylisoeugenole is converted by alcoholic alkali hydroxide into the nitro-compound, $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CH}\cdot\text{CHMe}\cdot\text{NO}_2$, which crystallises in golden-yellow needles melting at 72°. By zinc dust and acetic acid, it is reduced to a crystalline *oxime*, which yields, on hydrolysis with dilute sulphuric acid, the *ketone*,



an oil boiling at 195–200° under 11 mm. pressure and volatile in steam. The *semicarbazone* melts at 176°. The *nitrosochloride* melts and decomposes at 110°.

K. J. P. O.

Terpenes and Ethereal Oils. A New Case of Optical Isomerism. OTTO WALLACH (*Annalen*, 1904, 332, 337–351).—The 1:3-methylcyclohexanone (this vol., i, 424) has an optical activity, which is markedly influenced by the nature of the solvent; thus, in ethyl alcohol, $[\alpha]_D$ is +10.45°; in chloroform, +14.77°; in carbon tetrachloride, +11.86°; and in ether, +17.44°. The mean value is taken as +13.38° at 15°. The *oxime* obtained from this dextro-rotatory methylcyclohexanone is lævorotatory, having $[\alpha]_D$ –42.05° in ether at 21°. When benzoylated, this *oxime* yields a mixture of two *benzoyl* derivatives, which differ not only in crystalline form and melting point, but also in rotatory power; the α -*compound*, which is formed in much the larger proportion, is obtained free from the β -variety by repeated crystallisation from methyl alcohol and then from petroleum, and forms large, transparent, hemimorphic, monoclinic, pyroelectric crystals $[a:b:c=0.8796:1:0.9752; \beta=115^\circ 57' 3'']$,

melting at 96—97° and having $[\alpha]_D +19.97^\circ$ in ethereal solution at 22°. The β -compound can only be prepared with difficulty, and crystallises from petroleum in thin prisms melting at 82—83°, belonging to the hemihedric rhombic system

$$[a : b : c = 0.72482 : 1 : 0.8641];$$

this substance is lævorotatory, having $[\alpha]_D -86.08^\circ$ in ethereal solution at 21°.

Both benzoyl derivatives yield the pure oxime (m. p. 43—44°); since the possibility of different chemical constitutions, or of their not being true oximes, $\begin{array}{c} \text{CHMe} \cdot \text{CH}_2 \cdot \text{C} \cdot \text{NOBz} \\ | \\ \text{CH}_2 - \text{CH}_2 \cdot \text{CH}_2 \end{array}$, but nitroso-derivatives,

$\begin{array}{c} \text{CHMe} \cdot \text{CH}_2 \cdot \text{CBz} \cdot \text{NO} \\ | \\ \text{CH}_2 - \text{CH}_2 \cdot \text{CH}_2 \end{array}$, when a second asymmetric carbon atom would be present, seems to be excluded, the stereoisomerism must be due to the nitrogen atom, and the two varieties must be *syn*- and *anti*-forms. Up to the present, no such case has been observed in which such an isomerism has been accompanied with different optical activity.

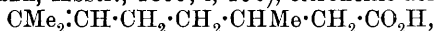
[With W. KEMPE.]—Although the lævorotatory 1:3-methylcyclohexanone has not been prepared, the inactive modification can be obtained. When the oxime is benzoylated, two inactive modifications are formed, which can be separated by crystallising from a mixture of ethyl acetate and petroleum; the α -compound, which exceeds the isomeride very largely in amount, forms monoclinic crystals $[a : b : c = 0.886 : 1 : 0.970; \beta = 117^\circ 21']$ melting at 105—106°; the β -compound crystallises in needles melting at 70—72°.

Although stereoisomeric oximes of unsaturated cyclic ketones are known, another example of a similar phenomenon in a saturated ketone has not hitherto been observed. 1:3-Methylcyclopentanone, which is powerfully dextrorotatory, yields a mixture of oximes, from which a product (the α -oxime) crystallising in prisms (from petroleum) and melting at 91—92.5° could be isolated; from the mother liquor, no substance with a constant melting point could be obtained; both the original crystals and the substance contained in the mother (the β -oxime) liquor have $[\alpha]_D$ about $+50^\circ$ in ethereal solution. On benzoylating the α -oxime, melting at 91—92.5°, a feebly dextrorotatory material, which melted at 60—61°, was obtained, but the β -oxime from the mother liquor also gave a benzoyl derivative melting at 60—61°; their rotations in ether were respectively $+29.77^\circ$ and $+34.64^\circ$.

Attempts were also made to obtain two benzoyl derivatives from *l*-menthoneoxime, but only one compound, which melted at 54° and had $[\alpha]_D 1.904^\circ$, was found. K. J. P. O.

[Carone and Fenchyl Alcohol.] IWAN KONDAKOFF (*J. pr. Chem.*, 1904, [ii], 69, 566—568).—The oxidation of Nikitin's carone (*J. Russ. Phys. Chem. Soc.*, 1904, 26, [6]) by potassium permanganate was due to the presence of carvenone. Nikitin's isomeric liquid fenchyl alcohol (*loc. cit.*) is *d*-*l*-fenchyl alcohol containing considerable quantities of fenchone. G. Y.

Complete Synthesis of Rhodinol, the Characteristic Alcohol of Essence of Roses. LOUIS BOUVEAULT and GOURMAND (*Compt. rend.*, 1904, 138, 1699—1701).—The authors have synthesised rhodinol, the characteristic alcohol of essence of roses (compare Bouveault and Barbier, *Abstr.*, 1896, i, 445). By reducing ethyl geranate (compare Barbier and Bouveault, *Abstr.*, 1896, i, 445, 637) by means of sodium and absolute alcohol (compare *Abstr.*, 1903, i, 730), or by reducing synthetical geranic acid by sodium and amyl alcohol (compare Tiemann, *Abstr.*, 1899, i, 190), citronellic acid,



is obtained, which boils at 146° under 10 mm. pressure, is converted into the ethyl ester boiling at 115° under 10 mm. pressure by heating with ethyl bromide and sodium ethoxide; this, on reduction with sodium and absolute alcohol, yields inactive (racemic) rhodinol, $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\text{OH}$, boiling at 110° under 10 mm. pressure and having a sp. gr. 0.877 at $0^\circ/4^\circ$. But for its optical inactivity, racemic rhodinol is identical with the rhodinol of essence of roses or pelargonium; its *pyruvate* is a colourless oil boiling at 143° under 10 mm. pressure, and forms a *semicarbazone* melting at 112° , soluble in methyl alcohol and sparingly so in ether (compare this vol., i, 465); the semicarbazone, similarly prepared from the active alcohol, has the same solubility and melting point and does not depress the melting point of the inactive compound. W. A. M.

Equilibrium between Chlorocamphor and Bromocamphor. MAURICE PADOA (*Atti R. Accad. Lincei*, 1904, [v], 13, i, 723—732).—Mixtures containing from 0 to 10 per cent. of chlorocamphor have freezing points slightly higher than that of pure bromocamphor; further increase of the proportion of chlorocamphor lowers the freezing point until about 20 per cent. of the chloro-compound is present, after which the melting point curve rises continually to a maximum again.

It is found that chlorocamphor and bromocamphor are completely isodimorphous, that is, they give two distinct series of mixed crystals in all proportions, one being monoclinic and the other cubic. A triple point exists at 75.6° , at which liquid, monoclinic and cubic crystals, all containing about 40 per cent. of bromocamphor, exist together.

T. H. P.

History of the Dicyclic Thujenes. IWAN L. KONDAKOFF (*J. pr. Chem.*, 1904, [ii], 69, 560—565. Compare *Abstr.*, 1902, i, 807; Tschugaeff, this vol., i, 515).—A criticism of Tschugaeff's work and a claim for priority. G. Y.

Matico Oil. HERMANN THOMS (*Arch. Pharm.*, 1904, 242, 328—344).—The oil examined was similar to that investigated by Fromm and van Emster (*Abstr.*, 1903, i, 188). The matico ether of these observers was a mixture of much dill-apiole with less parsley-apiole (Ciamician and Silber, *Abstr.*, 1888, 1100; 1896, i, 608). This mixture forms the bulk of the oil; also present are a *hydrocarbon* which boils at 121 — 130° under 13 mm. pressure and solidifies at -18° , and a

small amount of a *phenol ether* which yields a *bromo-derivative* melting at 123—124°. The bromo-derivative prepared from the lowest boiling fraction of the oil, which contained the least *apiole*, had relatively the highest melting point and percentage of bromine and the lowest percentage of methoxyl. Fromm and van Emster's *maticoic acid* was a mixture of *parsley-apiolic acid* with *dill-apiolic acid*; the latter melts at 151°. There is no longer any reason to suppose that three carbon atoms are lost as a result of the bromination, the bromo-derivative not having been formed from the "*matico ether*" (*apiole*) at all, but from the *phenol ether*.

These results are confirmed by Fromm, who acknowledges that his *matico-aldehyde* must have been a mixture of *dill-* and *parsley-apiole-aldehydes*, and his *homomaticoic acid* a mixture of the two corresponding *homo-apiolic acids*, as yet unknown in the pure state. C. F. B.

Decomposition of the Colloid Molecule of Caoutchouc and its Conversion into a Cyclic Hydrocarbon. RUDOLF DITTMAR (*Monatsh.*, 1904, 25, 464—474. Compare Abstr., 1902, i, 386; Harries, Abstr., 1902, i, 811).—Para-rubber is best purified by successive and repeated extraction with acetone, dilute potassium hydroxide, and water. After drying over sulphuric acid, the caoutchouc is soluble in fused paraffin, hot benzaldehyde, or quinoline.

The yellow, amorphous substance formed by oxidation of caoutchouc with fuming nitric acid is probably 3:6- or 5:6-dinitrodihydrocuminic acid. It is soluble in glacial acetic acid, acetone, or quinoline. After repeated solution and reprecipitation by ether, the solubility diminishes and a brown, polymeric(?) substance, insoluble in ethyl acetate, is obtained. The *alkali* salts, $C_{10}H_{11}O_6N_2M'$, are red, amorphous substances, and are soluble in water. The *methyl* ester, $C_9H_{11}O_4N_2 \cdot CO_2Me$, formed by the action of sodium methoxide on the acid in methyl alcoholic solution, is obtained as a red powder, which, when heated, swells up like mercuric thiocyanate. The acetyl anhydride, $C_9H_{11}O_4N_2 \cdot CO \cdot OAc$, is an orange-red powder and melts at 72°.

When heated with stannous chloride and hydrochloric acid in a sealed tube at 100°, the dinitro-compound is reduced to *diaminodihydro-p-cuminic acid*, which is obtained as a dark brown powder. G. Y.

Decomposition of Paracaoutchouc by Ozone. CARL D. HARRIES (*Ber.*, 1904, 37, 2708—2711).—When a chloroform solution of paracaoutchouc is oxidised with ozone and the solvent removed, a vitreous mass is obtained which possesses all the properties of an ozonide (this vol., i, 361). It has the composition $(C_{10}H_{10}O_6)_2$ or $(C_{10}H_{16}O_6)_3$, dissolves readily in alcohol, ethyl acetate, acetic acid, or benzene, may be purified by solution in ethyl acetate and precipitation with light petroleum, and, when boiled for a short time with water, yields hydrogen peroxide and a substance which gives the reaction of a keto-aldehyde or dialdehyde (Abstr., 1898, i, 232; 1902, i, 345). When boiled for a longer time with water, the hydrogen peroxide oxidises the aldehydes, and from the product thus obtained *lævulic acid* and an *acid* melting at 195° have been isolated. Oxalic acid is not formed. The acid melting at 195° appears to be a succinic acid.

The grouping $\begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{C} \end{array} > \text{C} : \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe} : \text{CH} \cdot \text{C}$ in the molecule of paracacoutchouc is suggested.

All ozonides emit rays which affect a photographic plate more readily than ozone itself. J. J. S.

Colophonia Elemi from Colophonia Mauritiana. ALEXANDER TSCHIRCH and OTTO SAAL (*Arch. Pharm.*, 1904, 242, 348—351. Compare Abstr., 1902, i, 812).—The sample examined came from the Mauritius, and had acid number 36 and saponification number 63. From its solution in ether, one per cent. aqueous ammonium carbonate extracted amorphous *α-isocolelemic acid*, $\text{C}_{37}\text{H}_{56}\text{O}_4$, which melted at 120—122°. One per cent. aqueous sodium carbonate then extracted acids, from a solution of which in a mixture of methyl and ethyl alcohols *coleleminic acid*, $\text{C}_{39}\text{H}_{56}\text{O}_4$, melting at 215°, crystallised; whilst amorphous *β-isocolelemic acid*, $\text{C}_{37}\text{H}_{56}\text{O}_4$, melting at 120°, remained in solution. The remaining solution, when distilled with steam, yielded an *essential oil*, boiling chiefly at 170—175°; the residue yielded crystals of *colamyrin*, $\text{C}_{30}\text{H}_{50}\text{O}$ (which was separated by benzylation, &c., into *α-* and *β-*amyrins), and amorphous *coleleresen*, $(\text{C}_{15}\text{H}_{24}\text{O})_n$, melting at 75—77°. A *bitter-principle* and *bryoidin* were also present.

In 100 parts of the drug there were contained: *α-isocolelemic acid*, 10; *coleleminic acid*, 2; *β-isocolelemic acid*, 8; *colamyrin*, 25—30; *coleleresen*, 30—35; *essential oil*, 3; *bitter-principle* and *bryoidin*, traces; plant remains and impurities, about 10. C. F. B.

Tacamahaca Elemi. ALEXANDER TSCHIRCH and OTTO SAAL (*Arch. Pharm.*, 1904, 242, 352—365. Compare Abstr., 1902, i, 812).—A number of samples of Tacamahaca resin were examined by moistening a little of each under the microscope with cold alcohol and noting whether or not any crystalline residue remained after the amorphous part had dissolved. One representative of each class was then examined in greater detail (compare also following abstract).

The specimen containing crystalline constituents came from the Philippines; it had acid number 35.5 and saponification number 65.2. From a solution of the resin in ether, 1 per cent. aqueous ammonium carbonate extracted amorphous *α-isotacelemic acid*, $\text{C}_{37}\text{H}_{56}\text{O}_4$, which melts at 120—121° and yields a monopotassium salt when treated with cold potassium hydroxide solution, a dipotassium salt on heating. One per cent. aqueous sodium carbonate then extracts acids, from a solution of which *tacelemic acid*, $\text{C}_{37}\text{H}_{56}\text{O}_4$ (molecular weight determined), melting at 215°, crystallises, whilst amorphous *β-isotacelemic acid*, $\text{C}_{37}\text{H}_{56}\text{O}_4$, melting at 120°, remains dissolved; both these acids resemble that just described in their reaction with an alkali. By distillation of the remaining solution with steam, an *essential oil* was obtained, boiling chiefly at 170—175°. From the residue, crystalline *tacamyryn*, $\text{C}_{30}\text{H}_{50}\text{O}$, was obtained; this was identical with amyryn from other sources: it melted at 170°, and its benzoyl derivative was separated into a mixture in about equal quantities of *α-* and *β-*benzoates, melting at 191—192° and 228—229° respectively, from which *α-* and

β -amyryns were regenerated, with melting points 181° and 192° . There remained amorphous *taceleresen*, $(C_{15}H_{24}O)_n$, melting at 75° . A *bitter principle* is present in the resin also.

The amyryn, $C_{30}H_{50}O$, is oxidised by permanganate in glacial acetic acid to monobasic *amyrrinic acid*, $C_{29}H_{47}\cdot CO_2H$ (molecular weight determined), which melts at $126-127^\circ$. From the behaviour of amyryn when oxidised (compare also Vesterberg, Abstr., 1892, 290) it is presumably a primary alcohol, $C_{29}H_{47}\cdot CH_2\cdot OH$. *Taceleresen* yields only oxalic and picric acids, in addition to amorphous products, when it is heated with nitric acid of sp. gr. 1.34; no camphoric or camphoronic acid is formed.

In 100 parts of the resin are contained: α -isotacelemic acid, 5; tacelemic acid, 2; β -isotacelemic acid, 3; essential oil, 2; tacamyryn, 30-35; *taceleresen*, 30-35; *bitter-principle*, 0.5; impurities, 15.

C. F. B.

Genuine Tacamahac of Commerce. ALEXANDER TSCHIRCH and OTTO SAAL (*Arch. Pharm.*, 1904, 242, 395-400).—The sample examined was of unknown origin, but may be taken as typical of those Tacamahaca resins which are entirely amorphous (compare preceding abstract); it melted at $85-87^\circ$ and had acid number 8.8, saponification number 36.4. From a solution of the resin in ether, 1 per cent. aqueous ammonium carbonate extracted amorphous *tacamahic acid*, $C_{43}H_{72}O_2$, melting at 95° . One per cent. aqueous sodium carbonate then extracted amorphous *tacamaholic acid*, $C_{15}H_{25}O_2$; this melts at $104-106^\circ$ and is monobasic. The remaining solution, when distilled with steam, yielded an *essential oil* boiling for the most part at $170-175^\circ$, whilst amorphous *takoresen* remained behind; this was separated into α - and β -*takoreses*, respectively insoluble and soluble in dilute alcohol of sp. gr. 0.892; the first, $C_{21}H_{33}O$, melts at $93-95^\circ$, the second, $C_{15}H_{25}O$, at 82° . A *bitter-principle* was also present, and when the resin is dissolved in ether, *tacamahaca gum*, $C_6H_{10}O_5$, remained undissolved. Evidently the substance does not belong to the group of elemi resins.

In 100 parts of the resin are contained: gum, 3; *tacamahic acid*, 0.5; *tacamaholic acid*, 0.5; essential oil, 3; α -*takoresen*, 50; β -*takoresen*, 30; *bitter-principle*, 0.5; impurities, 10. C. F. B.

Resins of the Elemi Group. ALEXANDER TSCHIRCH and OTTO SAAL (*Arch. Pharm.*, 1904, 242, 366-373).—A summary of the results obtained hitherto (Abstr., 1902, i, 812; 1903, i, 430; this vol., i, 332, 758). The resin acids in general may be referred to two groups: *eleminic acids*, with the formula $C_{39}H_{56}O_4$, and *elemic acids*, $C_{27}H_{56}O_4$. The *isoelemenic acids* are extracted by 1 per cent. aqueous ammonium carbonate, are amorphous, and melt at 75° ; the *eleminic acids* are extracted by 1 per cent. aqueous sodium carbonate, are crystalline, and melt at 215° . The *isoelemic acids* are extracted by 1 per cent. aqueous ammonium or sodium carbonate, are amorphous, and melt at 120° ; the *elemic acids* are extracted by 1 per cent. aqueous sodium carbonate or potassium hydroxide and are crystalline, melting at 215° , or amorphous, melting at 120° .

Generally the resins melt between 70° and 77° , and vary not inconsiderably in composition, approximating, however, to that required by $C_{15}H_{24}O$, the formula of an oxysequitepene. C. F. B.

Rutin from Rue (*Ruta Graveolens*). N. WALIASCHKO (*Arch. Pharm.*, 1904, 242, 225—254).—Rutin was extracted from the dry herb by repeated boiling with water; it formed a yellow, crystalline powder melting at $188-190^{\circ}$ and dissolved in 200 parts of cold, 7800 of boiling, water. It has the composition $C_{27}H_{30}O_{16} \cdot 3H_2O$, but easily loses $1H_2O$ in the air. When it is boiled with 10 per cent. nitric acid, it yields oxalic acid and a nitro-compound resembling picric acid. Boiling with 1 per cent. sulphuric acid hydrolyses it to quercetin, rhamnose, and dextrose.

Rutinquercetin is identical with the quercetin formed from quercitrin, and both substances form identical acetyl, ethyl, and acetyethyl derivatives. Rutinquercetin is a yellow, crystalline powder with the composition $C_{15}H_{10}O_7 \cdot 2H_2O$; it melts and decomposes at 310° . *Penta-acetylquercetin*, $C_{15}H_5O_7Ac_5$, melts at $191-192^{\circ}$. *Tetraethylquercetin*, $C_{15}H_6O_7Et_4$, melts at 121° and forms a yellow monopotassium derivative; *acetyltetraethylquercetin*, $C_{15}H_5O_7Et_4Ac$, melts at $152-153^{\circ}$. The last substance yields a mixture of di- and tri-ethylquercetins when it is hydrolysed; when this mixture is boiled with ethyl iodide and alcoholic potassium hydroxide, *triethylquercetin*, $C_{15}H_7O_7Et_3$, is formed; this is pale yellow, melts at $123-124^{\circ}$, and forms a yellow dipotassium derivative. In the ethylation of quercetin with ethyl iodide and alcoholic potassium hydroxide there are formed, in addition to the tetraethyl derivative, yellow *prisms* melting at 116° , possibly $C_{15}H_7O_7Et_3$, $C_{15}H_6O_7Et_4$, and yellowish-white spherical aggregates melting at 110° .

When quercetin in warm methyl-alcoholic solution is mixed with methyl sulphate and potassium hydroxide is added gradually, yellow *trimethylquercetin*, $C_{15}H_7O_7Me_3$, melting at 154° , is formed together with small quantities of two other yellow substances melting at 240° and 175° respectively. The trimethyl derivative forms a yellow potassium derivative, little soluble in alcohol and decomposed by water; if this is mixed with methyl sulphate in a mortar, *pentamethylquercetin*, $C_{15}H_5O_7Me_5 \cdot H_2O$, is formed; this melts at 148° and forms no potassium derivative.

The quercetin from rutin also agrees with that from quercitrin in yielding phloroglucinol and protocatechuic acid when fused with potassium hydroxide.

From the product of the hydrolysis of rutin with 1 per cent. sulphuric acid, after separation of the quercetin, rhamnose was isolated in the pure state and identified carefully. There remained an uncrystallisable syrup, which was identified with dextrose. The amount of quercetin formed in the hydrolysis of rutin, and of methylfurfural phloroglucide obtained (from the rhamnose) when rutin is distilled with 12 per cent. hydrochloric acid and phloroglucinol added to the distillate, and the rotation of the liquid left after hydrolysis, all harmonise with the equation $C_{27}H_{30}O_{16} + 3H_2O = C_{15}H_{10}O_7$ (quercetin) +

$C_6H_{14}O_6$ (rhamnose) + $C_6H_{12}O_6$ (glucose) as expressing the hydrolysis of rutin.

Rutin can be acetylated with acetic anhydride and methylated with methyl sulphate, but in neither case would the derivative crystallise.

The seeds of *Ruta graveolens* contain, in addition to rutin, an alkaloid (choline?), the *aurichloride* of which contains Au 45.4, Cl 31.6 per cent.; an acid (*rutic acid*), which was only obtained as a resinous solid; and a *resin*, which was obtained crystalline from alcohol.

Incidentally, it was found that Seliwanoff's reaction for lævulose (Abstr., 1887, 459), or more generally for all ketoses (Neuberg, *Zeit. physiol. Chem.*, 1900, 31, 566), is given by the syrups that are obtained in the hydrolysis of quercitrin, rutin, and robinin, although these only contain respectively rhamnose, rhamnose and glucose, and rhamnose and galactose in appreciable quantity. C. F. B.

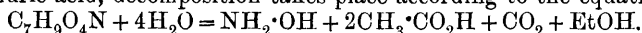
Saponin Substances of Dioscorea Tokoro Makino. J. HONDA (*Chem. Centr.*, 1904, ii, 118—119; from *Arch. exp. Path. Pharm.*, 1904, 51, 211—226).—The roots of *Dioscorea Tokoro Makino*, or the Japanese Oni-Tokoro or Tokoro, contain two saponin substances, dioscin and dioscorea sapotoxin. *Dioscin*, $C_{24}H_{38}O_{10} \cdot 3H_2O$, extracted from the roots by means of 96 per cent. alcohol, crystallises from absolute alcohol in white needles which have a silky lustre and melt at 247—250°. Dioscin is readily soluble in alcohol, methyl alcohol, or glacial acetic acid, sparingly so in hot water, chloroform, amyl alcohol, or acetone, very sparingly so in cold water, and insoluble in ether or light petroleum. The alcoholic solution is dextrorotatory, and the aqueous solution froths readily. It forms a yellow solution in concentrated sulphuric acid, which becomes successively reddish-yellow, dark red, and violet. Potassium dichromate and potassium permanganate give green and violet colorations respectively with solutions in concentrated sulphuric acid. Dioscin dissolves in Frohde's reagent, forming a yellow solution which turns violet. Warm concentrated nitric acid gives a yellow solution, and on boiling with concentrated hydrochloric acid the liquid froths and white flakes are formed. When boiled with dilute acids, dioscin yields a dextrorotatory sugar together with a compound which crystallises from alcohol in leaflets, and is readily soluble in ether, alcohol, methyl alcohol, or light petroleum. The *acetyl* derivative is an amorphous substance and is readily soluble in ether, chloroform, benzene, alcohol, or glacial acetic acid. *Sapotoxin*, $C_{23}H_{38}O_{10}$, isolated from the roots by means of lead acetate and magnesia, is a white, deliquescent, amorphous powder, melts at 172°, and is soluble in alcohol or methyl alcohol, but only very sparingly so in ether, chloroform, amyl alcohol, acetone, light petroleum, or carbon disulphide. It is readily soluble in water; a solution containing 1 part in 200,000 of water froths. The aqueous solution is levorotatory. With concentrated sulphuric acid, potassium permanganate, potassium dichromate, and nitric acid it gives the same reactions as dioscin, and with hot concentrated hydrochloric acid it develops a ruby-red coloration. By the action of dilute acids, with the exception of nitric acid, acetic acid, and phosphoric acid, it forms flocculent precipitates on boiling. When boiled with acids, a compound which has reducing

properties is formed together with a substance which is readily soluble in alcohol or ether, but insoluble in water. The *benzoyl ester* is a colourless, amorphous substance and is readily soluble in ether, chloroform, or benzene.

Dioscin and sapotoxin have a poisonous action on fish, that of the former being the stronger. Solutions of sapotoxin also destroy tænia. The hæmolytic action of dioscin is greater than that of any other saponin; sapotoxin has only a feeble action. Amœbæ, when immersed in a solution of sapotoxin, are quickly reduced to a mass of detritus. Dioscin is tasteless, and neither induces sneezing nor a burning sensation in the nose, but it has an irritating action on the conjunctiva. Solutions of sapotoxin which contain only 1 part in 10,000 of water have an intensely bitter taste. Dioscin, when administered to dogs *per os*, acts as a slight emetic. Subcutaneous injection of either compound causes local irritation in the case of frogs, and feeble paralysis of a central nature with complete immobility of the muscles; with warm-blooded animals only local irritation is caused. E. W. W.

Substantive Dyes containing Sulphur. FRITZ POLLAK (*Zeit. Farb. Text. Ind.*, 1904, 3, 233—237, 253—258).—A *résumé* of the subject, with an attempt at classification. W. A. D.

Action of Hydroxylamine on Ethyl Dimethylpyrnedicarboxylate. F. CARLO PALAZZO (*Gazzetta*, 1904, 34, i, 458—482. Compare Abstr., 1902, i, 816).—The action of hydroxylamine on ethyl dimethylpyrnedicarboxylate yields a compound, $C_7H_9O_4N$, which separates from water in shining crystals containing H_2O and melting at 166° . It acts towards potassium hydroxide as a monobasic acid, and forms a *silver salt*, $C_7H_8O_4NAg$, and an *ethyl ester*, $C_7H_8O_3N \cdot OEt$, which crystallises from water in silky needles, melting at 80° , and is readily hydrolysed. On heating the compound or its salts with dilute sulphuric acid, decomposition takes place according to the equation:

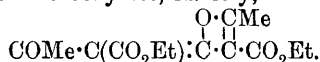


Oxidation with permanganate yields nitrous, nitric, acetic, and oxalic acids.

The compound probably has the constitution

$$OH \cdot N : \overset{\overset{O \cdot CMe}{\parallel}}{C} \cdot C \cdot CO_2Et,$$

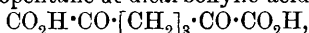
corresponding with the formula given by Conrad and Guthzeit for ethyl dimethylpyrnedicarboxylate, namely,



T. H. P.

Researches in the Pyran[1 : 4-Pent-furfuran] Series. EDMOND E. BLAISE and H. GAULT (*Compt. rend.*, 1904, 139, 137—139).—Ethyl oxalacetate condenses with formaldehyde in the presence of piperidine to form the compound $CH_2[CH(CO_2Et) \cdot CO \cdot CO_2Et]_2$, which crystallises from ether, melts at $80-81^\circ$, gives a red coloration with ferric chloride, combines readily with 1 mol. of water or hydrogen sulphide, gives crystalline derivatives with phenylhydrazine or hydrazine, and loses

carbon dioxide on hydrolysis with hydrochloric acid, forming *diketo-pimelic acid* [α -diketopentane- α -dicarboxylic acid],



in the form of colourless crystals melting at 127° , and converted into pimelic acid by hydrogenation and reduction, and into the dinitrile of glutaric acid by decomposing the dioxime with boiling water. Diketo-pimelic acid forms crystalline metallic salts, hydrazone, phenylhydrazone, semicarbazone, oxime, and condensation products with aniline or potassium hydrogen sulphite and yields *pyran-2:6-dicarboxylic acid*, $\text{CH}_2 < \begin{smallmatrix} \text{CH}:\text{C}(\text{CO}_2\text{H}) \\ \text{CH}:\text{C}(\text{CO}_2\text{H}) \end{smallmatrix} > \text{O}$; on dehydration, the new acid crystallises in colourless needles, decomposes at 250° , and yields crystalline salts and esters. M. A. W.

Synthesis of Galangin. STANISLAUS VON KOSTANECKI, VICTOR LAMPE, and JOSEF TAMBOR (*Ber.*, 1904, 37, 2803—2806).—The synthesis of 5:7-dihydroxyflavonol is described and the identity of this substance with the naturally-occurring galangin established.

When 2'-hydroxy-4':6'-dimethoxychalkone (Kostanecki and Tambor, *Abstr.*, 1899, i, 892) in alcoholic solution is heated with dilute hydrochloric acid, it undergoes transformation into 5:7-dimethoxyflavanone, $\text{C}(\text{OMe})\text{:CH}\cdot\text{C}\begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix}\cdot\text{CHPh}$, $\text{CH}\text{:C}(\text{OMe})\cdot\text{C}\begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix}\cdot\text{CO}\text{CH}_2$, which separates from alcohol in colourless, prismatic needles and melts at $146\text{--}147^\circ$; it forms yellow solutions with alcoholic sodium hydroxide and with concentrated sulphuric acid. Its 3-isonitroso-derivative, prepared by the action of amyl nitrite and hydrochloric acid, crystallises from benzene in yellow needles and melts and decomposes at $175\text{--}177^\circ$.

5:7-Dimethoxyflavonol crystallises from alcohol in yellow prisms and melts at $177\text{--}178^\circ$; it forms an intensely-yellow sodium salt; its solution in concentrated sulphuric acid is greenish-yellow and exhibits green fluorescence. Its *acetyl* derivative separates from dilute alcohol in white needles and melts at $192\text{--}193^\circ$.

5:7-Dihydroxyflavonol (galangin), $\text{C}(\text{OH})\text{:CH}\cdot\text{C}\begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix}\cdot\text{CPh}$, $\text{CH}\text{:C}(\text{OH})\cdot\text{C}\begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix}\cdot\text{CO}\cdot\text{C}\begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix}\cdot\text{OH}$, prepared by boiling 5:7-dimethoxyflavonol with concentrated hydriodic acid, contains $1\text{H}_2\text{O}$; it crystallises from dilute alcohol in yellowish-white needles and melts at $217\text{--}218^\circ$. For the natural product, Jahns gives $214\text{--}215^\circ$ and Testoni $219\text{--}221^\circ$. The colour reaction of the synthesised product, when dissolved in concentrated sulphuric acid, was identical with that of the natural product. The *acetyl* derivative, prepared both from the natural and from the synthesised product, crystallises from alcohol in silky needles and melts at $140\text{--}142^\circ$.

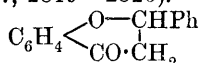
A. McK.

An Isomeride of Galangin. F. DOBRZYŃSKI and STANISLAUS VON KOSTANECKI (*Ber.*, 1904, 37, 2806—2809).—7:8-Dimethoxyflavanone is best prepared by the action of dilute sulphuric acid on an alcoholic solution of 2'-hydroxy-3':4'-dimethoxychalkone, obtained by the action of benzaldehyde on gallacetophenonedimethylether.

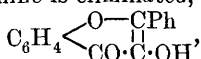
3-iso*Nitroso*-7 : 8-*dimethoxyflavanone*, prepared by the action of amyl nitrite and fuming hydrochloric acid on 7 : 8-dimethoxyflavanone, crystallises from benzene in white needles and melts and decomposes at 166°. Its solution in dilute aqueous sodium hydroxide is yellow. When dissolved in acetic acid and then boiled with dilute sulphuric acid, hydroxylamine and 7 : 8-*dimethoxyflavonol* are formed; the latter separates from alcohol in yellow needles and melts at 203°; its solution in concentrated sulphuric acid is greenish-yellow; its *acetyl* derivative crystallises from alcohol in white plates and melts at 185°. When boiled with hydriodic acid, it is converted into 7 : 8-*dihydroxyflavonol*, which separates from dilute alcohol in pale yellow needles and melts at 249°. Its solutions in alkalis are reddish-yellow; its solution in concentrated sulphuric acid is yellow. Its *acetyl* derivative crystallises from alcohol in white needles and melts at 210°.

A. McK.

Synthesis of Flavonol. STANISLAUS VON KOSTANECKI and W. SZABRAŃSKI (*Ber.*, 1904, 37, 2819—2820).—When flavanone,



(compare this vol., i, 684), is acted on by amyl nitrite and hydrochloric acid, it is converted into 3-isonitrosoflavanone, $\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{O}-\text{CHPh} \\ \diagdown \text{CO}\cdot\text{C}:\text{NOH} \end{array}$, which melts and decomposes at 158—159°. When boiled with dilute mineral acids, hydroxylamine is eliminated, whilst *flavonol*,

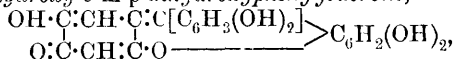


is produced; it crystallises from alcohol in yellow needles and melts at 169—170°. It forms a yellow solution when warmed with aqueous sodium hydroxide; on cooling, the sparingly soluble *sodium* salt separates in yellow needles. The solution of flavonol in concentrated sulphuric acid exhibits an intense violet fluorescence. Its *acetyl* derivative separates from dilute alcohol in glistening needles and melts at 110—111°.

A. McK.

Condensation of Hydroxyquinol with Aldehydes. CARL LIEBERMANN and SIMON LINDENBAUM (*Ber.*, 1904, 37, 2728—2737. Compare this vol., i, 443).—2 : 3 : 7-Trihydroxy-9-methylfluorone may readily be obtained in the form of its sulphate by mixing an alcoholic solution of hydroxyquinol and paracetaldehyde with 15 per cent. sulphuric acid. It forms orange-red needles, and on solution in alcohol containing a few drops of sulphuric acid and precipitation with water yields the free base in the form of dark red needles with a metallic lustre. The *acetyl* derivative forms pale yellow needles, melts at 225—228°, and its solutions do not exhibit fluorescence.

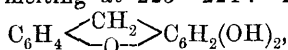
2 : 3 : 7-Trihydroxy-9-m-p-dihydroxyphenylfluorone,



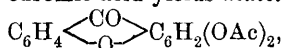
is obtained as the *sulphate*, $(\text{C}_{19}\text{H}_{12}\text{O}_7)_2\cdot\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$, when an aqueous alcoholic solution of hydroxyquinol and procatechuic aldehyde is left in

contact with concentrated sulphuric acid for some 5 weeks. When boiled with water, the sulphate is decomposed and yields a precipitate of the *base* in the form of small, orange-red needles with a metallic lustre. It melts above 300° and is sparingly soluble in the usual solvents. Its alcoholic solution has a strong, yellowish-green fluorescence, and it dissolves in alkalis, yielding red solutions with a pale red fluorescence. The *penta-acetyl* derivative melts at $227-231^{\circ}$.

Hydroxyquinol and *p*-hydroxybenzaldehyde in presence of sulphuric acid yield 2:3:7-*trihydroxy-9-p-hydroxyphenylfluorone sulphate* in the form of an intense yellow, voluminous precipitate. The *base* forms orange-red needles with a metallic lustre, and the *tetra-acetyl* derivative melts at $242-243^{\circ}$. 2:3:7-*Trihydroxy-9-o-hydroxyphenylfluorone*, obtained from salicylaldehyde and hydroxyquinol, yields a *sulphate* in the form of compact, glistening, red needles; the *base* crystallises in brownish-red needles, is extremely readily soluble in alcohol, and yields an *acetyl* derivative melting at $223-224^{\circ}$. 2:3-*Dihydroxyxanthen*,



may be obtained from the mother liquor from which the sulphate separates. It crystallises from hot water in rose-coloured plates melting at $173-175^{\circ}$ and readily soluble in the common organic solvents. It also dissolves in alkali or concentrated sulphuric acid, but none of the solutions fluoresces. The *diacetyl* derivative crystallises in long, glistening needles, sinters at 100° , melts at 110° , and on oxidation with chromic acid yields *diacetoxyxanthone*,

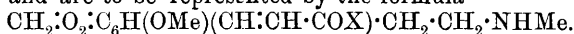


which crystallises in glistening needles melting at 186° . When treated with cold concentrated sulphuric acid, or when boiled with dilute alkali, it yields the corresponding *dihydroxyxanthone*, which crystallises from alcohol in long, yellow needles resembling anthraquinone. It melts at 294° , is sparingly soluble in chloroform, and solutions in organic solvents are practically colourless. Its solution in concentrated sulphuric acid fluoresces, and its solutions in alkalis have an intense yellow colour. It has practically no dyeing properties, and thus differs from the isomeric 3:4-dihydroxyxanthone (Graebe and Eichen-grün, Abstr., 1891, 706). Salicylaldehyde and resorcinol condense in aqueous alcoholic solution, and in the presence of sulphuric acid at 100° , yielding colourless needles which appear to be a mixture of two compounds, since, when acetylated, two *acetyl* derivatives are obtained. The one of these, $\text{C}_{13}\text{H}_7\text{O}_3\text{Ac}_2$, is insoluble in alcohol, crystallises in colourless, glistening plates, does not melt below 300° , and is sparingly soluble in the usual solvents.

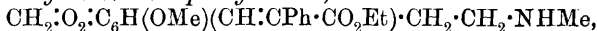
The second compound, which is isomeric, melts at $270-275^{\circ}$ and dissolves readily in the usual solvents. J. J. S.

Condensation of Cotarnine and of Hydrastinine with Ketones. CARL LIEBERMANN and A. GLAWE (*Ber.*, 1904, 37, 2738—2744. Compare this vol., i, 263).—Cotarnine and hydrastinine yield condensation products with most compounds containing a methylene group between two carbonyl groups; they also react with

coumarone, resorcinol, quinol, and other compounds, but not with meconine. Some of the condensation products are relatively stable; others, for example, those with ethyl malonate derivatives, are readily hydrolysed to their components. In many of the condensations, piperidine gives better yields than sodium carbonate solution. Most of the condensation products appear to have a hydrogen atom attached to nitrogen, and are to be represented by the formula



Ethyl anhydrocotarninephenylacetate,



crystallises from alcohol in colourless prisms melting at 91–92°. The *platinichloride* is precipitated as a yellow, flocculent mass and the *nitrate* as small and sparingly soluble needles.

Ethyl anhydrohydrastininphenylacetate melts at 85–86° and the *nitrate* is readily soluble.

Ethyl anhydrocotarninemalonate,



forms a colourless, crystalline powder melting at 73° and readily soluble in the usual organic solvents. On treatment with chloroplatinic acid, it is decomposed and yields cotarnine *platinichloride*. The *methiodide* crystallises in colourless needles melting at 201°.

Ethyl anhydrohydrastininemalonate melts at 55–57°, is readily soluble in alcohol, and is very unstable.

Anhydrocotarninecoumaron, $\text{C}_{12}\text{H}_{14}\text{O}_3\text{N}\cdot\text{C}_8\text{H}_5\text{O}$, is precipitated on the addition of light petroleum to its ethereal solution as a yellow, amorphous mass melting at 66–71°; the *platinichloride* is also amorphous. The corresponding *hydrastinine* derivative melts at 68–70° and dissolves in concentrated sulphuric acid to a violet-coloured solution.

Anhydrocotarnineresorcinol, obtained without the aid of a condensing agent, melts and decomposes at 220°, is only sparingly soluble in the usual solvents, but dissolves in dilute acids. The *hydrochloride* is somewhat sparingly soluble in hydrochloric acid and melts at 242°.

J. J. S.

Condensations with Cotarnine. F. KROFF (*Ber.*, 1904, 37, 2744–2750. Compare this vol., i, 263 and preceding abstract).—*Anhydrocotarnine acetylacetone*, $\text{C}_{17}\text{H}_{21}\text{O}_5\text{N}$, crystallises in colourless prisms melting at 98–99°; the *hydrochloride* crystallises in glistening, hygroscopic needles and the *platinichloride* in yellow needles. *Anhydrocotarnineacetonylacetone*, $\text{C}_{18}\text{H}_{23}\text{O}_5\text{N}$, melts at 147–149° and is readily soluble in alcohol or ether. *Ethyl anhydrocotarnineacetoacetate*, $\text{C}_{18}\text{H}_{23}\text{O}_6\text{N}$, crystallises in colourless needles melting at 59–60°. *Ethyl anhydrocotarninebenzoylacetate*, $\text{C}_{23}\text{H}_{24}\text{O}_6\text{N}$, melts at 100–102° and yields a *platinichloride* melting at 116–117°.

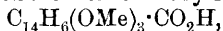
Ethyl anhydrocotarninecyanoacetate, $\text{C}_{17}\text{H}_{20}\text{O}_5\text{N}_2$, melts and decomposes at 95–96° and is extremely unstable. *Ethyl anhydrocotarnineethylacetoacetate*, $\text{C}_{20}\text{H}_{27}\text{O}_6\text{N}$, is an oil and yields a *hydrochloride* which crystallises in colourless needles. The corresponding *derivative* of ethyl benzylacetoacetate is also an oil.

Methyl iodide reacts in the cold with a methyl-alcoholic solution of

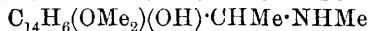
anhydrocotarnineacetophenone (this vol., i, 263), yielding a mixture of the corresponding hydriodide, which is readily soluble in water, and the *methiodide*, which crystallises from alcohol in colourless needles melting at 225—226°. If the mixture is not kept cool, the product is *anhydro-methylcotarnineacetophenone hydriodide*. This crystallises in long, colourless needles, melts at 171°, and is readily soluble in alcohol or water. The addition of alkali to the aqueous solution yields the *base*, $C_{21}H_{23}O_4N$, which melts at 78°. Anhydrocotarnineacetophenone, on treatment with acetic anhydride, yields an *acetyl* derivative, which crystallises in colourless needles melting at 139—140°; the *benzoyl* derivative melts at 107—108°. The *benzoyl* derivative of anhydrocotarnineacetone, obtained by direct benzoylation of anhydrocotarnineacetone or by the condensation of benzoylcotarnine (Roser, Abstr., 1890, 528), melts at 124°. These reactions indicate the presence of an NH group in anhydrocotarnine-acetone and -acetophenone.

J. J. S.

Constitution of Thebenine. ROBERT PSCHORR and CORNELIUS MASSACIU (*Ber.*, 1904, 37, 2780—2792. Compare Freund, Abstr., 1899, i, 307).—When thebaine is heated with hydrochloric acid, one of the methyl groups is hydrolysed and at the same time the tertiary is converted into a secondary base. Contrary to the observations of Freund, the methyl ether, methebenine, of thebenine is soluble in alkalis and has a phenolic character, although in dilute solutions it requires six mols. of alkali for dissolution; the third oxygen atom, not accounted for by the two methyl groups, is therefore phenolic and does not form part of a furane ring. Hence thebenine may be formulated as $OH \cdot C_{16}H_{10}(OMe)_2 \cdot NHMe$. The hydroxyl group cannot be methylated until the secondary nitrogen has been converted into a quaternary compound, but the product, $C_{16}H_{10}(OMe)_3NMe_3I$, when heated with alkali hydroxides, loses trimethylamine and gives a trimethoxyphenanthrene derivative, $C_{14}H_6(OMe)_3 \cdot CH:CH_2$, which was oxidised to trimethoxyphenanthrenecarboxylic acid,



proving that all three oxygen atoms of methebenine are directly linked to the phenanthrene nucleus. The formula



is suggested for thebenine.

Diacetylmethebenine, $C_{23}H_{15}O_5N$, prepared by the action of acetic anhydride on a cold alkaline solution of methebenine, was found to be identical with the compound which Freund obtained by boiling with sodium acetate and acetic anhydride, a process which Freund assumed to be accompanied by a splitting of the furane ring, which can hardly be supposed to occur under the milder conditions now employed. Under similar conditions, benzoyl chloride gives a *dibenzoyl* derivative, $C_{33}H_{29}O_5N$, which crystallises from alcohol in needles and melts at 159° (corr.).

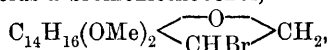
Dimethebeninmethine methiodide, $C_{16}H_{10}(OMe)_3 \cdot NMe_3I$, prepared by the action of potassium iodide on the methylsulphate, crystallises from alcohol in bundles of needles and melts at 247° (corr.). The

methylsulphate, $C_{16}H_{10}(OMe)_3 \cdot NMe_3 \cdot SO_4Me$, crystallises in colourless needles, sinters at 268° , and melts at 270° (corr. 277°).

Trimethoxyvinylphenanthrene, $C_{16}H_9(OMe)_3$, prepared by heating either of the preceding compounds with potassium hydroxide, crystallises from alcohol in well-formed, pale yellow tablets and melts at 122.5° (corr.). The *picrate* forms red, quadrilateral tablets and melts at 110° .

Trimethoxyphenanthrenecarboxylic acid, $C_{18}H_{16}O_5$, crystallises from acetic acid in small, yellow needles and melts at $219-221^\circ$ (corr.).

Boiling in acetic acid solution, or with a little hydrochloric acid in alcoholic solution, converts the vinyl derivative into Freund's methebenol, a compound which contains no hydroxyl group and is formulated as $C_{14}H_6(OMe)_2 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{smallmatrix} \text{CH}_2$, and bromination of the vinyl derivative yields a bromomethebenol,



which crystallises from chloroform in needles and melts at $148-149^\circ$ to a liquid which decomposes at $205-207^\circ$. T. M. L.

isoCreatinine and its Identity with Creatinine. E. POULSSON (*Chem. Centr.*, 1904, ii, 30—31; from *Arch. exp. Path. Pharm.*, 1904, 51, 227—238).—Thesen's *isocreatinine* (Abstr., 1898, i, 387) is impure creatinine which contains a yellow dye. The latter may be removed by heating with animal charcoal or by purification by means of the sulphate. The substance prepared according to Thesen's directions gives all the reactions of ordinary creatinine and does not exhibit any peculiar or characteristic behaviour. The flesh of cod contains 0.2, of halibut 0.17, and of mackerel 0.22 per cent. of creatinine, whilst 0.055 per cent. is present in lean beef.

Creatinine tartrate, $(C_4H_7ON_3)_2 \cdot C_4H_6O_6$, crystallises in needles, decomposes at $207-209^\circ$, and is readily soluble in water, but only sparingly so in alcohol. *Creatinine oxalate*, $(C_4H_7ON_3)_2 \cdot C_2H_2O_4$, crystallises in prisms and is soluble in water, but only very sparingly so in alcohol. E. W. W.

isoCreatinine. G. KORNDÖRFER (*Arch. Pharm.*, 1904, 242, 373—379).—The author has arrived independently at the same conclusion as Poulsson (preceding abstract), namely, that the *iso*-creatinine of Thesen (Abstr., 1898, i, 387) is identical with the creatinine of urine, &c. "*isoCreatinine*" was prepared from the flesh of the cod, and obtained colourless by passage through the hydrochloride or platinichloride; it was found to be identical with creatinine from urine in a number of physical properties and chemical reactions.

C. F. B.

Damascenine. OSKAR KELLER (*Arch. Pharm.*, 1904, 242, 299—327. Compare Pommerehne, Abstr., 1899, i, 964; 1900, i, 684; 1901, i, 289; this vol., i, 685).—When the hydrochloride of damascenine, $C_9H_{11}O_3N_3$, is treated with bromine in alcoholic solution and

the solution eventually diluted with ether, crystals of a salt, $C_9H_{11}O_3NBr_2 \cdot HBr$, separate; these melt at $198-201^\circ$.

Damascenine is converted into a *monacetyl* derivative, $C_9H_{10}O_3N \cdot Ac$, melting at $203-204^\circ$, when its hydrochloride is boiled with acetic anhydride.

Damascenine is transformed, when it is boiled with alcoholic potash or other alkalis, into a monobasic acid, damasceninic acid, isomeric with damascenine (molecular weight determined), and still containing a methoxyl group; some salts of this substance, which has the character of an amino-acid, have been described already. The *hydrobromide*, $C_9H_{11}O_3N \cdot HBr \cdot H_2O$, melting at $204-206^\circ$, the *sulphate*, $C_9H_{11}O_3N \cdot H_2SO_4 \cdot H_2O$, melting at $209-210^\circ$, and the amorphous *silver* and green, crystalline *copper* salt, $(C_9H_{10}O_3N)_2Cu \cdot \frac{1}{2}H_2O$, melting at $215-217^\circ$, have been analysed; other copper salts seem capable of existence. A *methyl* ester appears to exist, of which the *hydrochloride*, $C_9H_{10}O_3NMe \cdot HCl \cdot H_2O$, melts at $199-200^\circ$ when dried.

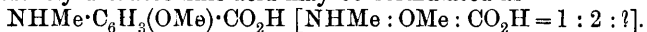
Bromine in alcoholic solution converts damasceninic acid into a substance, $C_9H_{11}O_3NBr_2$, which melts at $206-208^\circ$. Acetic anhydride converts it into the same acetyl compound as was obtained from damascenine itself; this acetyldamascenine does not form an additive compound with methyl iodide, and therefore probably contains the acetyl group attached to the nitrogen atom.

Methyl iodide converts damasceninic acid into the same hydriodide as is obtained in similar circumstances from damascenine itself; the free *base*, $C_9H_{10}O_3NMe$, melts at $118-119^\circ$. The further action of methyl iodide leads to the formation of a quaternary *iodide*, $C_9H_{10}O_3NMe \cdot MeI \cdot H_2O$, melting at $175-176^\circ$ (at $164-166^\circ$ when dried); the corresponding *hydrochloride* (not analysed) melts at $185-186^\circ$; the hydroxide appears to undergo no decomposition when its aqueous solution is distilled.

Nitrous acid converts both damascenine and damasceninic acid into a *nitroso-derivative*, which melts at $151-152^\circ$.

When damasceninic acid is boiled for a comparatively short time with hydriodic acid (b. p. 127°), 1 mol. proportion of methyl iodide is evolved; this is followed by a second if the heating is prolonged. When damascenine is heated with hydriodic acid for several hours at $150-160^\circ$, *o*-aminophenol is obtained together with a little of a *hydriodide*; the latter contains I 55.6 per cent. and melts at $213-214^\circ$; after it has been crystallised from water, a *compound* free from iodine and melting at $240-260^\circ$ is obtained.

Evidently damasceninic acid may be formulated as



C. F. B.

Conversion of Ephedrine into ψ -Ephedrine. F. FLAECHER (*Arch. Pharm.*, 1904, 242, 380-383).—By heating ephedrine with 5 per cent. hydrochloric acid at $170-180^\circ$ for 5 hours it was converted into the "*isoephedrine*" of Nagai (*Chem. Zeit.*, 1890, 441); this, however, is found to be nothing else but the ψ phedrine of Ladenburg and Oelschlägel (*Abstr.*, 1889, 1020).

C. F. B.

Poisonous Constituent of the Alpine Salamander, *Salamandra atra*. FRITZ NETOLITZKY (*Chem. Centr.*, 1904, ii, 130—131; from *Arch. exp. Path. Pharm.*, 1904, 51, 118—129).—*Samandatrine*, prepared from the alcoholic extract of the macerated flesh and slimy secretions of *Salamandra atra*, forms a clear yellow syrup which is very readily soluble in hot amyl alcohol, readily so in ether or chloroform, and very sparingly so in cold water or alcohol. It is distinguished from the alkaloids samandarine and samandaridine, from *S. maculosa*, by its solubility in ether. The solutions of samandatrine have an alkaline reaction and are precipitated by alkaloidal reagents. When boiled for a few minutes with concentrated hydrochloric acid, a faint violet coloration is formed which becomes bluish-red in 24 hours, and by repeatedly evaporating with the acid a blue, amorphous residue is left. Concentrated sulphuric acid dissolves samandatrine, forming a pale yellow solution which, after several days, becomes pale violet. The *sulphate*, $(C_{21}H_{37}O_3N_2)_2H_2SO_4$?, crystallises in white needles, has a very bitter taste, and is sparingly soluble in water. About 1 milligram of the sulphate can be prepared from one salamander. The physiological action of the alkaloid resembles that of the alkaloids of *S. maculosa* (compare Faust, *Abstr.*, 1899, i, 380). The results of experiments on cold-blooded animals show that the alkaloid probably attacks the central nerve system.

E. W. W.

Oxidation of Pyrrole to Maleimide. GIUSEPPE PLANCHER and F. CATTADORI (*Atti R. Accad. Lincei*, 1904, [v], 13, i, 489—492).—

Maleimide, $NH \begin{array}{c} \diagup CO \cdot CH \\ | \\ \diagdown CO \cdot CH \end{array}$, prepared by the oxidation of pyrrole, separates from ethyl acetate in faintly yellow crystals melting at 93° ; it readily sublimes in shining, slender plates and has a pungent odour, while its vapours attack the mucous membrane of the nose and eyes. With ammoniacal silver nitrate solution, it yields a crystalline precipitate, which separates from water in colourless plates. When treated with bromine water in the light, it yields the dibromide melting at about 226° .

T. H. P.

Trichloropyrrole. V. GIROLAMO MAZZARA and A. BORGO (*Gazzetta*, 1904, 34, i, 414—420).—The trichloropyrrole (*Abstr.*, 1904, i, 614), formed by the action of sulphuryl chloride ($3\frac{1}{2}$ mols.) on pyrrole (1 mol.), is obtained in almost theoretical yield when the products of the reaction are distilled in a current of steam under 100 mm. pressure, the receiver being covered with a black cloth. Trichloropyrrole undergoes change extremely readily when subjected to the action of light or air. When gradually added to concentrated nitric acid of sp. gr. 1.48, it yields the chloromaleimide obtained by Ciamician and Silber (*Abstr.*, 1884, 293) by the action of chlorine on succinimide, together with small quantities of dichloromaleimide apparently formed from traces of tetrachloropyrrole admixed with the trichloro-compound.

As the reaction between sulphuryl chloride and pyrrole only pro-

ceeds readily in the absence of moisture, freshly purified materials should be employed, as well as absolutely anhydrous alcohol.

T. H. P.

Bromotrichloromethylpyrrole and Chlorobromomaleic Methylimide. VI. GIROLAMO MAZZARA (*Gazzetta*, 1904, 34, i, 482—491. Compare preceding abstract).—2 : 3 : 5-Trichloro-4-bromo-1-methylpyrrole, $C_5H_3NCl_3Br$, prepared by passing bromine vapour slowly into 2 : 3 : 5-trichloro-1-methylpyrrole suspended in water, or by the action of bromine on a solution of 2 : 3 : 5-trichloro-1-methylpyrrole in glacial acetic acid, crystallises from alcohol in slender, white, silky needles, melting at 120° . It volatilises with difficulty in a current of steam, sublimes with slight decomposition at 100° , and is soluble in sulphuric acid developing a red coloration; in benzene, it exhibits normal cryoscopic behaviour.

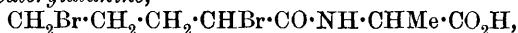
The action of cold fuming nitric acid on this compound yields *chlorobromomaleic methylimide*, $NMe \begin{smallmatrix} \diagup CO \cdot CBr \\ | \\ \diagdown CO \cdot CCl \end{smallmatrix}$, which sublimes in shining, pale yellow laminae, composed of long, flattened needles melting at 103° .

The oxidation of 2 : 3 : 4 : 5-tetrachloro-1-methylpyrrole with either bromine or nitric acid yields dichloromaleic methylimide (see this vol., i, 614), which melts at 89° .

T. H. P.

Synthesis of Polypeptides. III. Derivatives of Pyrrolidine-2-carboxylic Acids. EMIL FISCHER and UMETARO SUZUKI (*Ber.*, 1904, 37, 2842—2848. Compare this vol., i, 652).—*α*-Dibromovaleryl chloride, formed by the action of phosphorus pentachloride on *α*-dibromovaleric acid (Willstätter and Ettlinger, *Abstr.*, 1903, i, 362), is a colourless oil, which boils at 122 — 127° under 13—15 mm. pressure.

α-Dibromovalerylalanine,



is formed when dibromovaleryl chloride and alanine are shaken with sodium hydroxide in aqueous solution and the product acidified. It crystallises in colourless needles, sinters at 110° , and melts at 113 — 116° (corr.), and is easily soluble in alcohol, ether, or benzene, moderately so in cold water. The substance may be a mixture of two isomerides. The action of ammonia on dibromovalerylalanine leads to the formation of *prolylalanine*,

$\begin{smallmatrix} CH_2 \cdot CH_2 \\ | \\ CH_2 - NH \end{smallmatrix} > CH \cdot CO \cdot NH \cdot CHMe \cdot CO_2H$, which

crystallises in colourless, glistening, microscopic plates and melts, with the formation of the anhydride, when rapidly heated at 225 — 230° . When heated with hydrochloric acid, it yields alanine and pyrrolidine-

α-carboxylic acid. The *anhydride*, $CH_2 \begin{smallmatrix} \diagup CH_2 \cdot N - CO \cdot CHMe \\ | \\ CH_2 \cdot CH \cdot CO \cdot NH \end{smallmatrix}$, crystallises in small, colourless prisms and melts at 126 — 129° . When heated with cupric oxide and water, the dipeptide forms a blue *copper* salt which is easily soluble in water. The anhydride does not give this reaction.

G. Y.

Pyrogenic Changes in the Pyrrole Series. AME PICTET (*Ber.*, 1904, 37, 2792—2797).—[With A. STEINMANN.]—When 1-methyl-

pyrrole is distilled through a tube heated to a dull red, it is converted into 2-methylpyrrole, which boils at 144.5—145.5° under 717 mm. pressure, has sp. gr. 0.9446 at 15°/4°, n_D 1.50353 at 16°. A small amount of pyridine was also produced.

[With G. LONG.]—1-o-Tolylpyrrole, $C_{11}H_{11}N$, is a colourless oil which does not solidify when cooled and boils at 246°.

1-p-Tolylpyrrole, $C_{11}H_{11}N$, separates from dilute alcohol in pearly flakes, melts at 82°, and boils at 252° (corr.) under 728.5 mm. pressure.

1- α -Naphthylpyrrole, $C_{14}H_{11}N$, separates from dilute alcohol in colourless needles, melts at 42°, and boils above 360°.

1- β -Naphthylpyrrole separates from dilute alcohol in minute scales, melts at 170°, and boils above 360°.

2-o-Tolylpyrrole is an oil which boils at 284°. 2-p-Tolylpyrrole forms colourless flakes, melts at 153°, and boils at 294°.

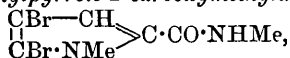
2- β -Naphthylpyrrole forms pearly scales and melts at 155°.

[With S. RUDSTEIN.]—1-Benzoylpyrrole, $C_{11}H_9ON$, prepared by the action of benzoyl chloride on potassium pyrrole, is a yellow oil, boils at 276° (corr.) under 715 mm. pressure, and is converted at a dull red heat into 2-benzoylpyrrole. T. M. L.

Bromo-derivatives of Pyrrole-2-carboxylic Acid and 1-Methylpyrrole-2-carboxylic Acid. EUGÈNE KHOTINSKY and AMÉ PICTET (*Ber.*, 1904, 37, 2798—2802) — 4:5-Dibromopyrrole-2-carboxylamide, $\begin{array}{c} \text{CBr} \cdot \text{CH} \\ | \\ \text{CBr} \cdot \text{NH} \end{array} > \text{C} \cdot \text{CO} \cdot \text{NH}_2$, prepared by the action of bromine on pyrrole-2-carboxylamide, crystallises from acetic acid in colourless flakes melting at 145—146° and containing 1 mol. of acetic acid; the hydrated amide, $C_5H_4ON_2Br_2 \cdot H_2O$, separates from hot water in colourless flakes and melts at 158°. Nitric acid oxidises the amide to dibromomaleimide.

4:5-Dibromopyrrole-2-carboxylic acid, $C_5H_3O_2NBr_2 \cdot H_2O$, prepared by heating the amide with alcoholic potash at 110—115°, crystallises from water in flakes and melts at 110°; the anhydrous acid melts at 158°.

4:5-Dibromo-1-methylpyrrole-2-carboxymethylamide,



crystallises from dilute alcohol in long, silky needles and melts at 137°. The acid, $C_6H_5O_2NBr_2$, crystallises from alcohol in white needles, darkens and decomposes when heated, and is oxidised by nitric acid to dibromomaleic methylimide.

Bromo-1-methylpyrrole-2-carboxymethylamide, $C_7H_9ON_2Br$, crystallises from hot water in colourless needles and melts at 112°. The acid, $C_6H_6O_2NBr$, crystallises from dilute alcohol in pearly scales and decomposes without melting.

Tribromo-1-methylpyrrole-2-carboxymethylamide, $C_7H_7ON_2Br_3$, crystallises from dilute acetic acid or alcohol in glistening flakes and melts at 176°. The acid, $C_6H_4O_2NBr_3$, crystallises from alcohol in white needles and decomposes without melting. T. M. L.

Decomposition of Phenyl Esters by Organic Bases. KARL AUWERS (*Annalen*, 1904, 332, 214—226).—When piperidine acts on the acetates of dibromo-*o*-hydroxybenzyl bromide and of tribromo-hydroxy-*m*-xylylene bromide, not only is the bromine of the side-chain replaced, but also the acyl group is removed, even when the action takes place in the presence of a solvent or at a low temperature. Such a reaction has never been observed in the case of primary bases, and investigation has shown that this decomposition depends on the strength of the secondary base and on the nature of the acyl group.

The following secondary bases were investigated: piperidine, diethylamine, piperazine, tetrahydroquinoline, and methylaniline; of these, piperidine exerts by far the most powerful action. Only when the reaction between piperidine and dibromo-*o*-acetoxybenzyl bromide takes place at -12° to -15° is the *dibromo-*o*-acetoxybenzylpiperidine*, $\text{OAc} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{CH}_2 \cdot \text{C}_5\text{NH}_{10}$, produced; it forms triclinic prisms melting at $86-87^{\circ}$. The *hydrochloride* (m. p. $222-223^{\circ}$) and the *hydrobromide* (decomposing at 250°) are formed when dibromo-*o*-hydroxybenzylpiperidine is warmed respectively with acetyl chloride or bromide. The benzoate, $\text{OBz} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{CH}_2 \cdot \text{C}_5\text{NH}_{10}$, which crystallises in needles melting at $110-111^{\circ}$, is obtained by benzoylating the free phenol, and can also be prepared, in contrast to the acetate, by the action of piperidine at the ordinary temperature in benzene solution on the benzoate of dibromo-*o*-hydroxybenzyl bromide; but in the absence of a solvent and at a higher temperature, dibromo-*o*-hydroxybenzylpiperidine is formed.

Diethylamine, which stands next to piperidine in activity, does not effect the hydrolysis of dibromo-*o*-acetoxybenzyl bromide in the presence of a solvent at a temperature below $40-50^{\circ}$, but when heated under pressure at 100° , or when the acetate is dissolved in excess of diethylamine, *dibromo-*o*-hydroxybenzyl-diethylamine* is formed and crystallises in needles melting at $141-142^{\circ}$.

Methylaniline and tetrahydroquinoline are unable to effect the decomposition; when methylaniline is allowed to act on dibromo-*o*-acetoxybenzyl bromide in the absence of a solvent and at 100° , only *dibromo-*o*-acetoxybenzylmethylaniline*, $\text{OAc} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{CH}_2 \cdot \text{NMePh}$, is produced, crystallising in needles melting at 91° . In boiling xylene, tetrahydroquinoline acts in the same way, yielding *dibromo-*o*-acetoxybenzyl-tetrahydroquinoline*, which crystallises in needles melting at 105° ; the free *phenol*, prepared by mixing the two components in benzene solution, crystallises in needles melting at $113-114^{\circ}$, and is readily acetylated.

Piperazine removes the acetyl group when it is heated with the dibromoacetoxy-derivative in boiling xylene solution, the compound $(\text{OH} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{CH}_2)_2\text{C}_4\text{N}_2\text{H}_8$ being produced; it crystallises in needles melting at $199-201^{\circ}$. The *hydrobromide* of tetrabromodihydroxy-dibenzylpiperazine is precipitated on mixing solutions of dibromo-hydroxybenzyl bromide and piperazine, and is converted into the phenol, which forms crystals melting at $240-242^{\circ}$; when cautiously acetylated in the presence of pyridine it yields the acetyl derivative just mentioned, but when boiled with acetic anhydride it is converted into the diacetate of dibromosaligenin (m. p. 71°). K. J. P. O.

Complex-formation. II. Pyridine Complexes. HANS EULER (*Ber.*, 1904, 37, 2768—2773).—Determinations of the stability of pyridine metallic complexes by means of measurements of solubility and *E.M.F.* show that these complexes are much less stable than those containing ammonia or alkylamines. This is shown by the dissociation constants tabulated below:

| Metal. | Pyridine. | <i>K.</i> | Ammonia. | <i>K.</i> |
|---------|-------------------|----------------------|-----------------------------------|----------------------|
| Ag..... | AgPy ₂ | 4×10^{-5} | Ag(NH ₃) ₂ | 5×10^{-8} |
| Ni..... | NiPy ₂ | 2.5×10^{-1} | Ni(NH ₃) ₄ | 1.1×10^{-5} |
| Cd..... | CdPy ₂ | 1.4×10^{-1} | Cd(NH ₃) ₄ | 3.2×10^{-4} |
| Zn..... | ZnPy ₂ | 2.8×10^{-1} | Zn(NH ₃) ₄ | 1.6×10^{-3} |

T. M. L.

Thio- and Seleno-derivatives of *N*-Alkyl-pyridones and -lutidones. AUGUST MICHAELIS and A. HÖLKEN (*Annalen*, 1904, 331, 245—264).—Starting from α -halogen derivatives of pyridine, thio- and seleno-derivatives of pyridones have been prepared by the action of potassium hydrosulphide and hydroselenide. In a similar manner, the corresponding lutidones have been obtained from γ -chlorolutidines. Thus, from the methiodide of α -iodopyridine, *N*-methyl- α -selenopyridone, $\begin{array}{c} \text{CH}:\text{CH}:\text{C} \\ | \quad | \\ \text{CH}:\text{CH}:\text{NMe} \end{array} \text{---} \text{Se}$, and from the methiodide of

γ -chlorolutidine, *N*-methyl- γ -thiolutidone, $\begin{array}{c} \text{CH}:\text{CMe} \\ \diagdown \quad \diagup \\ \text{C} \quad \text{S} \\ \diagup \quad \diagdown \\ \text{CH}:\text{CMe} \end{array} \text{---} \text{NMe}$, were

respectively obtained. These substances yield alkyl iodide derivatives, which, on heating, lose alkyl iodide and are converted into methylthiol derivatives of pyridine or lutidine, isomeric with *N*-methylthio- or seleno-compounds. By the action of chlorine they are converted into trioxides analogous to the thiopyrine trioxides (compare p. 780).

(I) *Derivatives of 1-Methyl-1:2-pyridone.*—1:2-Thio-1-methylpyridone, $\begin{array}{c} \text{CH} \text{ CH}:\text{C} \\ | \quad | \\ \text{CH}:\text{CH}:\text{NMe} \end{array} \text{---} \text{S}$, separates when a hot concentrated solution of

the methiodide of α -iodopyridine is added to the calculated quantity of 20 per cent. potassium hydrosulphide, hydrogen sulphide being at the same time evolved; it forms pale yellow needles or prisms melting at 89°, and, when boiled with concentrated hydrochloric acid, is converted into 1-methyl-1:2-pyridone (compare Gutbier, *Abstr.*, 1901, i, 96). It reacts with methyl iodide, the methyl group becoming attached to the sulphur, and the iodine to the nitrogen; the compound forms needles melting at 155—156°; the corresponding methyl chloride compound forms white crystals melting at 97°. The *platini-chloride* forms reddish-yellow crystals. When distilled, methyl iodide is eliminated and 2-methylthiolpyridine (m. p. 197°) formed (compare Marekwald, Klemm, and Trabert, *Abstr.*, 1900, i, 456).

1-Methyl-1:2-selenopyridine, prepared in a similar manner to the sulphur compound, crystallises in brownish-yellow needles melting at 79—80°, and is less stable than the thiopyridone. The *methiodide*

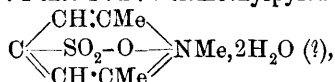
crystallises in white needles melting at 186° , and the *methochloride* in needles melting at 86° ; the *platinichloride* forms yellowish-brown prisms melting at 201° . When the methiodide is distilled, α -methyl-selenolpyridine, $\text{CH} \begin{smallmatrix} \text{CH} \cdot \text{CH} \\ \text{CH} = \text{N} \end{smallmatrix} \text{C} \cdot \text{SeMe}$, is obtained as a colourless liquid, with an odour resembling mercaptan, boiling at 212° ; it is soluble in acids and forms a very hygroscopic hydrochloride.

II. *Derivatives of 1-Alkyl-1:4-lutidones*.—The methiodide of γ -chlorolutidine was prepared from γ -lutidone, which was first converted into γ -chlorolutidine by Conrad and Epstein's method (Abstr., 1887, 501), and then the latter heated with methyl iodide under pressure for 6 hours at 100° ; the *methiodide* crystallises with $2\text{H}_2\text{O}$ and melts at 228 – 230° , and, when anhydrous, at 233 – 234° . When γ -chlorolutidine is heated with ethyl iodide for 6 hours at 120° , the ethiodide of γ -iodolutidine is obtained as colourless leaflets melting at 239 – 240° .

1:4-Thio-1:3:6-trimethylpyridine, prepared from the methiodide just described and potassium hydrosulphide, crystallises in yellow needles melting at 267 – 268° . It forms a very unstable, yellow, crystalline additive product with sulphur dioxide. The *hydrochloride* crystallises in needles melting at 233 – 234° ; the *methiodide* crystallises in needles melting at 236° ; the *platinichloride* forms red prisms melting at 234° .

1:4-Thio-2:6-dimethyl-1-ethylpyridine was obtained in a similar manner to the methyl compound and forms yellow needles melting at 248° ; the *methiodide* forms white crystals melting and decomposing at 154° ; the *methochloride* melts at 136° . On distilling the methiodide of either of these thio-1-alkyl-lutidones, alkyl iodide is eliminated and 4-methylthiolutidine (m. p. 51°) formed, identical with the substance prepared by Marckwald (*loc. cit.*).

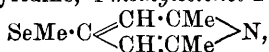
The trioxide of 1:4-thio-1:2:6-trimethylpyridine,



is prepared by passing chlorine into an aqueous suspension of the thiolutidine, and forms rhombic crystals, which carbonise without melting on heating and are indifferent towards both acids and alkalis.

1:4-Seleno-1:2:6-trimethylpyridine, prepared from the methiodide of γ -chlorolutidine and potassium selenide, crystallises in brown needles melting at 268° and is decomposed by boiling with dilute acids; the *methiodide* forms colourless needles melting and decomposing at 219° ; the *methochloride* melts at 210° , and the *platinichloride*, which crystallises in red crystals, at 224° . The corresponding ethyl compound, 1:4-seleno-2:6-dimethyl-1-ethylpyridine, forms brownish-red needles melting at 254° ; the *methiodide* crystallises in colourless needles melting at 155° , and the *methochloride* at 126° .

On distilling the methiodide of either the 1-methyl or the 1-ethyl-4-seleno-2:6-dimethylpyridine, 4-methylselenol-2:6-dimethylpyridine,



is obtained; it forms crystals melting at 70° ; the *hydrochloride* melts

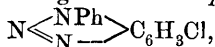
at 110°, and the *platinichloride*, which crystallises in brownish-red prisms, at 252°.

K. J. P. O.

Carbazoles. FRITZ ULLMANN [with E. DELETRA and D. KOGAN] (*Annalen*, 1904, 332, 82—104).—This paper is mainly a fuller account of work previously published (this vol., i, 270). In this communication, an account is given of the preparation of chlorocarbazoles and of naphthacarbazoles.

Carbazole, $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix}$, is prepared by distilling phenaziminobenzoic acid with three to four times its weight of lime, and melts at 238°.

3-Chlorocarbazole, $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_3\text{Cl} \\ \text{C}_6\text{H}_4 \end{smallmatrix}$, is obtained thus: 4-chloro-2-nitro-1-diphenylamine, $\text{NHPh} \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{NO}_2$, is prepared by heating for 10 hours 1:4-dichloro-2-nitrobenzene with aniline and anhydrous sodium acetate; it forms orange-red or reddish-brown crystals melting at 61°. When reduced with stannous chloride and hydrochloric acid, 4-chloro-2-amino-1-diphenylamine is obtained in colourless needles melting at 82°, and is converted by diazotising into 4-chlorophenaziminobenzene,



which crystallises in colourless needles melting at 142°. When heated alone, it becomes 3-chlorocarbazole, which forms white, silvery crystals melting at 201.5°. 2-Chlorocarbazole is prepared by heating for 1 hour at its melting point chlorophenaziminobenzene (Ernst, Abstr., 1891, 299), and crystallises in leaflets melting at 244°; it dissolves in sulphuric acid to a yellow solution, which becomes bluish-green on addition of nitric acid.

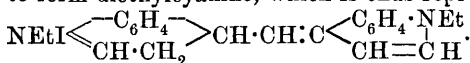
1:2-Naphthacarbazole, $\text{NH} \begin{smallmatrix} \text{C}_{10}\text{H}_6 \\ \text{C}_6\text{H}_4 \end{smallmatrix}$, prepared by the distillation of phenaziminonaphthalene (Zincke and Campbell, Abstr., 1890, 787), crystallises in colourless leaflets melting at 134.5—135° and forms colourless solutions which have a blue fluorescence; it dissolves in sulphuric acid with a yellow coloration, which becomes yellowish-green on addition of nitric acid. This compound is probably identical with the material obtained by Schopff (Abstr., 1895, i, 107) by distilling naphthacarbazolecarboxylic acid with zinc dust, although he records the melting point as 120°. The benzoyl derivative melts at 191°. 2'-Methyl-1:2-naphthacarbazole is obtained from *p*-tolyl naphthylenediamine, which is converted, on diazotisation, into *p*-tolylaziminonaphthalene, $\text{N} \begin{smallmatrix} \text{N}(\text{C}_6\text{H}_4\text{Me}) \\ \text{N} \end{smallmatrix} \text{---} \text{C}_{10}\text{H}_6$, forming colourless crystals melting at 145°. When distilled, the compound last mentioned passes into the carbazole, which forms crystals melting at 181°; its solutions are colourless, but have a blue fluorescence; the *picrate* crystallises in red needles melting at 212°.

K. J. P. O.

Constitution of Cyanine Dyes. A. MIETHE and GILBERT BOOK (*Ber.*, 1904, 37, 2821—2824. Compare this vol., i, 622).—*Lepidine ethiodide*, $\text{C}_{10}\text{H}_{19}\text{N} \cdot \text{EtI}$, prepared from lepidine and ethyl iodide, separates from alcohol in yellow crystals and melts at 142°.

By the action of potassium hydroxide (2 mols.) on a mixture of quinoline ethiodide (2 mols.) and lepidine ethiodide (1 mol.), diethylcyanine, $C_{23}H_{25}N_2I$, is formed as dark green needles.

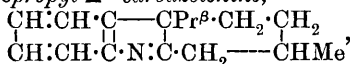
The mechanism of the action is supposed to be as follows. The quinoline ethiodide is converted into a quinolone; the hydrogen eliminated in this action converts the lepidine ethiodide into its dihydro-derivative, which interacts with the quinolone, with elimination of water, to form diethylcyanine, which is thus represented:



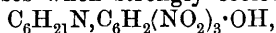
Di-iododiethylcyanine, $C_{23}H_{25}N_2I_3$, prepared by the action of iodine on diethylcyanine, separates from alcohol in olive-green, glistening crystals. It is not a periodide. A. McK.

Preparation and Transformations of Members of the Tetrahydrocarbazole Series. GIUSEPPE PLANCHER and O. CARRASCO (*Atti R. Accad. Lincei*, 1904, [v], 13, i, 632—636. Compare Plancher and Testoni, *Abstr.*, 1900, i, 562).—On condensation with alcoholic zinc chloride, menthone phenylhydrazone yields:

(1) 3-Methyl-6-isopropyl- Δ^N -carbazolenine,

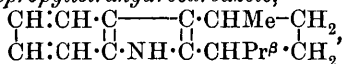


which forms a colourless mass boiling at $170\text{--}171^\circ$ under 14 mm. pressure, and crystallises when strongly cooled. Its *picrate*,



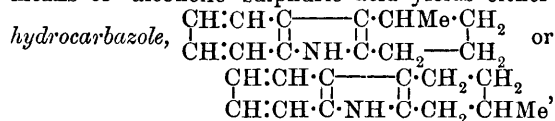
is pale yellow and melts at $166\text{--}167^\circ$. Its *methiodide* separates from a mixture of alcohol and ether in crystals melting and decomposing at $209\text{--}210^\circ$. Digestion of the methiodide with silver chloride yields the methochloride, which gives a crystalline aurichloride and platinichloride.

(2) 4-Methyl-1-isopropyltetrahydrocarbazole,

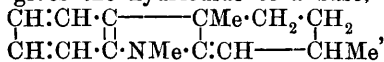


which boils at $202\text{--}204^\circ$ under 14 mm. pressure in a slightly impure state and yields a dark red *picrate* melting at $164\text{--}165^\circ$.

The condensation of β -methylketocyclohexanephénylhydrazone by means of alcoholic sulphuric acid yields either 4- or 2-methyltetra-

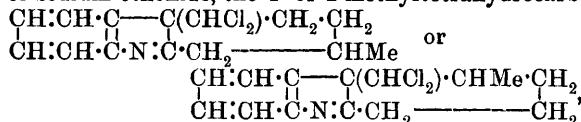


which gives well-formed rhombic crystals melting at $98\text{--}99^\circ$; it has no basic properties, smells faintly of indole, gives a red *picrate*, but does not give Angeli's reaction with anhydrous oxalic acid. With methyl iodide it gives the hydriodide of a base,



which yields a *picrate*, $C_{15}H_{19}N, C_6H_2(NO_2)_3OH$, crystallising in pale yellow leaflets melting at $143\text{--}144^\circ$. With chloroform, in presence

of sodium ethoxide, the 4- or 2-methyltetrahydrocarbazole gives a *base*,



which separates from light petroleum in very pale yellow plates melting at 125—126° and yields a *picrate* melting and decomposing at 162—163°.

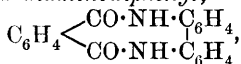
4- or 2-Methyltetrahydrocarbazole is readily reduced by phosphorus and hydriodic acid to the corresponding 4- or 2-methylcarbazoline, $\text{C}_{13}\text{H}_{17}\text{N}$, which is obtained in colourless, pleasant-smelling crystals melting at 102—103°; its *hydrobromide* melts at 230—231° and its *hydriodide* at 227—229°; its *platinichloride*, $(\text{C}_{13}\text{H}_{17}\text{N})_2\cdot\text{H}_2\text{PtCl}_6$, was analysed.

T. H. P.

Oxidation Products from *p*-Phenylenediamine. I. ERNST ERDMANN (*Ber.*, 1904, 37, 2776—2780).—When *p*-phenylenediamine is oxidised with potassium permanganate, the chief products are ammonia and carbon dioxide, $\text{C}_6\text{H}_8\text{N}_2 + 13\text{O} = 6\text{CO}_2 + 2\text{NH}_3 + \text{H}_2\text{O}$, but oxalic acid and hydrogen cyanide are also produced in small quantities.

T. M. L.

Action of Phthalic Anhydride on Aromatic Diamines. GUSTAV KOLLER (*Ber.*, 1904, 37, 2880—2883).—Phthalyl-4:4'-diaminodiphenyl, and not diphthalyliminodiphenyl (Bandrowski, *Abstr.*, 1884, 1015), is formed when phthalic anhydride and benzidine are boiled in aqueous suspension. *Phthalyl-4:4'-diaminodiphenyl*,



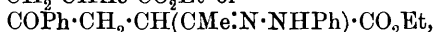
separates from its solution in boiling nitrobenzene in yellow, granular crystals, melts above 300°, and is insoluble in aqueous alkali hydroxides or dilute acids. When acted on by potassium nitrate in concentrated sulphuric acid solution, it yields a *mononitro*-derivative which crystallises in yellow needles, melts at 225°, and is hydrolysed by boiling aqueous sodium carbonate solution to 3-nitro-4'-phthalamino-4-amino-diphenyl, $\text{NH}_2\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. This crystallises in orange-coloured needles, melts at 140°, is easily soluble in aqueous sodium carbonate, and is hydrolysed by concentrated ammonia to *o*-nitrobenzidine, which crystallises in red needles and melts at 190°.

G. Y.

Ethyl $\alpha\beta$ -Diacylpropionates and Primary Hydrazines. WALTHER BORSCHÉ and M. SPANNAGEL (*Annalen*, 1904, 331, 298—318).—The action of hydrazine and primary hydrazines on ethyl $\alpha\beta$ -diacylpropionates, $\text{RCO}\cdot\text{CH}_2\cdot\text{CH}(\text{COR})\cdot\text{CO}_2\text{Et}$, has been investigated, the action of phenylhydrazine on ethyl phenacylacetoacetate, on ethyl acetonylacetoacetate, and on ethyl phenacylbenzoylacetoacetate being described in this communication.

When phenylhydrazine and ethyl phenacylacetoacetate are brought

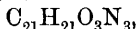
together in alcoholic solution, the *monophenylhydrazone* of the ester, $\text{NHPh}\cdot\text{N}:\text{CPh}\cdot\text{CH}_2\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$ or



separates in white needles melting at 152° ; the hydrazone is unstable, and, even in the pure state, when exposed to light becomes yellow, acquires an unpleasant odour, and gradually becomes a brown, oily mass; it gives no colour reaction with ferric chloride in alcoholic solution, and does not react either with phenylhydrazine or semicarbazide. After long heating in alcoholic solution, 1 mol. of water is lost and a ring is formed, *ethyl 1:5-diphenyl-2-methyl- $\Delta^{2:5}$ -dihydropyridazine-3-carboxylate*, $\text{N}\begin{smallmatrix} \text{CPh}\cdot\text{CH}_2 \\ \text{NPh}\cdot\text{CMe} \end{smallmatrix} \text{C}\cdot\text{CO}_2\text{Et}$, being produced; it

forms colourless crystals melting at $114\text{--}116^\circ$; the hydrazone is more rapidly changed into the pyridazine either by warming with acetic anhydride or by heating at $166\text{--}170^\circ$. The corresponding *acid* is obtained by hydrolysing the ester just described or by hydrolysing the hydrazone, and forms small crystals melting at $185\text{--}186^\circ$; if the ester of the pyridazine is fused with potassium hydroxide, aniline is eliminated, a methyl group oxidised, *2-phenylpyrrole-4:5-dicarboxylic acid* being produced, $\begin{smallmatrix} \text{C}(\text{CO}_2\text{H})\cdot\text{CH} \\ \text{C}(\text{CO}_2\text{H})\cdot\text{NH} \end{smallmatrix} \text{CPh}$; it crystallises in needles melting at 250° .

Ethyl phenacylacetoacetate and semicarbazide yield a cyclic semicarbazone, *ethyl 5-phenyl-2-methyl- $\Delta^{2:5}$ -dihydropyridazine-1-carbonamide-3-carboxylate*, $\text{CPh}\begin{smallmatrix} \text{CH}_2\cdot\text{C}(\text{CO}_2\text{Et}) \\ \text{N}\cdot\text{N}(\text{CO}\cdot\text{NH}_2) \end{smallmatrix} \text{CMe}$, which crystallises in needles melting at $254\cdot5^\circ$; it does not yield an acetyl derivative, and when warmed with alkali hydroxide the carbethoxy-group is alone hydrolysed, an *amide acid* being formed; it is crystalline and melts and decomposes at $247\text{--}248^\circ$. When the ester amide is boiled with aniline, *ethyl phenylmethyldihydropyridazinecarbonanilidecarboxylate*,



is obtained as colourless crystals melting at 192° ; it is also formed when ethyl phenacylacetoacetate is condensed with phenylsemicarbazide.

Ethyl acetonylacetoacetate forms with phenylhydrazine a viscid oil. Semicarbazide and the ester condense, 2 mols. of water being eliminated and *ethyl 2:5-dimethyl- $\Delta^{2:5}$ -dihydropyridazine-1-carbonamide-3-carboxylate*, $\text{CMe}\begin{smallmatrix} \text{CH}_2\cdot\text{C}(\text{CO}_2\text{Et}) \\ \text{N}\cdot\text{N}(\text{CO}\cdot\text{NH}_2) \end{smallmatrix} \text{CMe}$, produced; it forms colourless crystals melting at 230° .

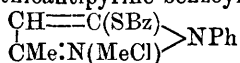
Ethyl phenacylbenzoylacetate (m. p. $69\text{--}72^\circ$; Paal, *Ber.*, 1888, 21, 1485, gives the melting point as $55\text{--}58^\circ$) reacts slowly with phenylhydrazine, yielding no definite products; semicarbazide gives a normal *semicarbazone*, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}:\text{CPh}\cdot\text{CH}_2\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$, which crystallises in colourless needles melting at $138\text{--}140^\circ$.

Ethyl benzoylacetate reacts readily with semicarbazide, yielding *3-phenylpyrazolone-1-carbonamide*, $\begin{smallmatrix} \text{CPh}=\text{N} \\ \text{CH}_2\cdot\text{CO} \end{smallmatrix} \text{N}\cdot\text{CO}\cdot\text{NH}_2$, which forms crystals melting at $184\text{--}185^\circ$.

K. J. P. O.

1-Phenyl-3-methylthiopyrazolone. AUGUST MICHAELIS and ROB. PANDER (*Ber.*, 1904, 37, 2774—2775).—1-Phenyl-3-methyl-5-thiopyrazolone, $\begin{array}{c} \text{CH:C(SH)} \\ \text{CMe:N} \end{array} \text{>NPh}$, prepared by hydrolysing the benzoyl derivative with dilute hydrochloric acid at 120°, separates from alcohol in well-formed crystals, melts at 109°, and boils with much decomposition at 294°. Methyl iodide reconverts it at once into the methiodide of

thioantipyrine. The benzoyl derivative, $\begin{array}{c} \text{CH:C(SBz)} \\ \text{CMe:N} \end{array} \text{>NPh}$, was obtained by distilling the thioantipyrine benzoyl chloride,



(*Abstr.*, 1902, i, 316), when a part of the methyl chloride is split off, whilst part of the substance is decomposed into benzoyl chloride and ψ -thioantipyrine; it crystallises from light petroleum in minute, white needles and melts at 93°. T. M. L.

Thiopyrine Series. AUGUST MICHAELIS [with ALBERT BESSON, WILLY MOELLER, and MAX KOBER] (*Annalen*, 1904, 331, 197—244. Compare *Abstr.*, 1901, i, 52).—Thiopyrine [thioantipyrine; 1-phenyl-2:3-dimethyl-2:5-thiopyrazole] is prepared by passing a current of carbon disulphide into a solution of sodium, potassium, or ammonium hydrosulphide, and adding later, or at the same time, a hot or cold aqueous or alcoholic solution of the methochloride or methiodide of phenylmethylchloropyrazole. It may also be obtained by treating an aqueous solution of antipyrine chloride with sodium thiosulphate, finally heating on the water-bath. The reactions may be represented as follows: $\text{C}_{11}\text{H}_{12}\text{N}_2\text{Cl}_2 + \text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 2\text{NaCl} + \text{C}_{11}\text{H}_{12}\text{N}_2\text{S}$, and $\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + \text{SO}_2 + \text{S} + \text{H}_2\text{O}$.

When distilled under the ordinary or reduced pressure, thiopyrine is converted into ψ -thiopyrine (5-methylthiol-1-phenyl-3-methylpyrazole), whereas antipyrine is, at higher temperatures, more stable than its isomeride. In physiological action, the two substances are alike.

Thiopyrine hydriodide forms transparent crystals sintering at 194° and melting at 202°, and on distillation changes into the hydriodide of the ψ -thiopyrine, which melts at 174—175°. The *ethiodide* forms thick plates melting at 158°; the *isopropylidide*, $\text{C}_{11}\text{H}_{13}\text{N}_2\text{S, Pr}^i\text{I, H}_2\text{O}$, forms white crystals, melting, when anhydrous, at 170—172°, and yielding, when distilled, 5-isopropylthiol-1-phenyl-3-methylpyrazole. The *isobutylidide* forms crystals melting at 117°, and the *allylidide* crystals melting at 125°. The *benzylchloride* is an oil, and the corresponding *iodide* forms white needles melting at 174—175°.

Both methylene and ethylene iodides act readily on thiopyrine, forming respectively bis-compounds, thus: $\text{CH}_2 \left[\text{S} \cdot \text{C} \begin{array}{c} \text{NPh} \cdot \text{N} \\ \text{CH} \cdot \text{CMe} \end{array} \right]_2$. The *methiodide* of 5-methylenebis-1-phenyl-3-methylthiopyrazole forms white needles melting and decomposing at 197°, the *methochloride* is crystalline and melts at 201°. The *methobromide* of 5-ethylenebis-

1-phenyl-3-methylthiopyrazole is crystalline and hygroscopic and melts at 176°.

Thiopyrine trioxide, $\begin{array}{c} \text{CMe} \cdot \text{NMe} \cdot \text{O} \\ | \\ \text{NPh} \\ | \\ \text{CH} = \text{CH} - \text{SO}_2 \end{array}$, is prepared by heating anti-pyrene chloride with sodium sulphite and crystallises in needles (with H₂O) from water.

Homologues of Thiopyrine.—Ethylthiopyrine (2:5-thio-1-phenyl-3-methyl-2-ethylpyrazole), $\begin{array}{c} \text{CMe} \cdot \text{NEt} \\ | \\ \text{NPh} \\ | \\ \text{CH} = \text{C} \end{array} \rangle \text{S}$, is prepared from the ethiodide of

5-iodo-1-phenyl-3-methylpyrazole, which is converted first into the ethochloride and then treated with potassium hydrosulphide in alcoholic solution (compare Michaelis and Pasternack, Abstr., 1899, i, 941, and Michaelis and Bindewald, Abstr., 1901, i, 52); it forms crystals melting at 171°, behaves towards ferric chloride as does thiopyrine, and with sulphur dioxide forms an additive product, C₁₂H₁₄N₂S₂SO₂, crystallising in yellow leaflets which melt and decompose at 113°. The methiodide forms crystals melting at 203°.

Ethylthiopyrine trioxide (ethylammonium 1-phenyl-3-methyl-2:5-pyrazolesulphonate), $\begin{array}{c} \text{CMe} \cdot \text{NEt} \cdot \text{O} \\ | \\ \text{NPh} \\ | \\ \text{CH} = \text{C} - \text{SO}_2 \end{array}$, is formed when chlorine is passed into an aqueous solution of ethylthiopyrine, and crystallises in leaflets melting and decomposing at 257°.

The allylbromide of 5-bromo-1-phenyl-3-methylpyrazole is obtained by heating chloropyrazole with allyl bromide under pressure, and forms colourless needles melting at 196°; the corresponding allylchloride is hygroscopic and melts at 182°. The allyliodide of 5-iodo-1-phenyl-3-methylpyrazole crystallises in needles melting at 203°, and the corresponding allylchloride forms crystals melting at 193–194°. Allylthiopyrine, prepared from the allylchloride, forms crystals melting at 123°, and, when treated with sulphur dioxide, yields a crystalline additive product melting at 92–95°; the methiodide forms crystals melting at 142°. By aqueous chlorine, allylthiopyrine is converted into chloro-

propylthiopyrine trioxide, $\begin{array}{c} \text{C} - \text{NPh} \\ || \quad \diagdown \\ || \quad \text{O} \cdot \text{SO}_2 \cdot \text{N} \cdot \text{CH}_2 \cdot \text{CHMeCl} \\ | \\ \text{CH} - \text{CMe} \end{array}$, which forms crystals melting and decomposing at 244°.

Methylthiopyrine (2:5-thio-1-phenyl-2:3:4-trimethylpyrazole) forms monoclinic crystals melting at 129°; the hydrochloride is very hygroscopic, and the platinichloride (with 2H₂O) is a flesh-coloured powder melting at 226° (compare Abstr., 1902, i, 315). It forms two additive products with sulphur dioxide; at the ordinary temperature, an orange-yellow, crystalline precipitate melting at 145–148°, and at 100° greenish-yellow, stable crystals, C₁₂H₁₄N₂S₂SO₂·H₂O, melting at 200–203°. The methiodide forms large, monoclinic crystals melting at 167°, which crystallise from water with H₂O. The methochloride crystallises in needles melting at 91°, and yields a platinichloride which

crystallises in reddish-brown leaflets melting at 256°. The *ethiodide* crystallises in colourless plates melting at 125°, and the *benzylchloride* forms crystals melting at 72°.

Methylthiopyrpyrine trioxide (*methylammonium 1-phenyl-3:4-dimethylpyrazolesulphonate*), $\begin{array}{c} \text{CMe:NMe}\cdot\text{O} \\ | \\ \text{NPh} \\ | \\ \text{CMe:C}-\text{SO}_2 \end{array}$, forms transparent, rhombic crystals melting and decomposing at 305°.

Dichloromethylthiopyrpyrine crystallises in hygroscopic, yellow needles, and the *dibromide* is a yellowish-red powder melting at 111°.

Pseudothiopyrpyrines.—On heating the iodoalkyl derivatives of thiopyrpyrines, two decompositions take place: alkyl iodide is eliminated and a 5-thioalkylpyrazole formed; and secondly, especially in the case of ethylthiopyrpyrine, ethyl iodide is eliminated and a ψ -thiopyrpyrine

produced, thus: $\begin{array}{c} \text{CMe:N(MeI)} \\ | \\ \text{CH=C(SET)} \end{array} > \text{NPh} = \text{EtI} + \begin{array}{c} \text{CMe:NMe} \\ | \\ \text{S} \\ | \\ \text{CH=C} \end{array} > \text{NPh}$, or

$\begin{array}{c} \text{CMe} \\ || \\ \text{CH:C(SMe)} \end{array} > \text{NPh}$. The ψ -thiopyrpyrines yield characteristic methiodides, are converted by oxidising agents into sulphones, and with halogen give additive products if a hydrogen atom is present in position 4; if an alkyl group occupies position 4, the group (SMe) is replaced by halogen. By a mixture of nitric and sulphuric acids, the phenyl group is nitrated. Concentrated hydrochloric acid causes the elimination of sulphur and methyl chloride and the formation of a pyrazole.

ψ -Thiopyrpyrine (5-methylthiol-1-phenyl-3-methylpyrpyrazole), best prepared by the repeated distillation of thiopyrpyrine, is a colourless liquid of pleasant odour boiling at 165–166° under 11 mm. and at 306–307° under 760 mm. pressure; the *hydrochloride* forms crystals with H₂O, is decomposed by water, and when dry melts at 103°. The *platinichloride* forms with 2H₂O red crystals melting at 160°. The *nitrate* forms hygroscopic crystals melting at 53–55°, and the *picrate* yellow needles melting at 77–78°. ψ -Thiopyrpyrine only combines with alkyl iodides when heated under pressure; the methiodide is identical with that obtained from thiopyrpyrine; the *ethiodide* forms white needles, the *isopropiodide* crystals with H₂O, which melt when anhydrous at 187°, and the *isobutyliodide* colourless crystals melting at 189–191°.

The *sulphone* of ψ -thiopyrpyrine (1-phenyl-3-methyl-5-methylsulphonepyrpyrazole), $\begin{array}{c} \text{CMe} \\ || \\ \text{CH:C(SO}_2\text{Me)} \end{array} > \text{NPh}$, is obtained when ψ -thiopyrpyrine, dissolved in acetic acid, is oxidised by potassium permanganate, dilute nitric acid, or hydrogen peroxide; it crystallises in needles melting at 89–90°. The *methiodide* forms crystals melting at 194°.

4-Bromo- ψ -thiopyrpyrine (4-bromo-5-methylthiol-1-phenyl-3-methylpyrpyrazole), prepared by brominating ψ -thiopyrpyrine in chloroform solution, crystallises in plates melting at 52°, and is also formed from 4-bromothiopyrpyrine. The *methiodide* forms crystals melting at 179°, and when heated with dilute sodium hydroxide yields mercaptan and antipyrine.

The corresponding *sulphone*, 4-bromo-1-phenyl-3-methyl-5-methylsulphonepyrazole, crystallises in white leaflets melting at 150—151°.

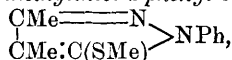
Nitro ψ-thiopyrine, prepared by treating ψ-thiopyrine with a mixture of nitric and sulphuric acids, crystallises in pale yellow leaflets melting at 135—136°.

Homo-ψ-thiopyrine, $\begin{array}{c} \text{CH}=\text{N} \\ | \\ \text{CH}:\text{C}(\text{SMe}) \end{array} > \text{NPh}$, is obtained as a yellow oil boiling at 142—143° under 14 mm. pressure, when the methiodide of homothiopyrine is distilled.

When the ethiodide of thiopyrine is distilled under the ordinary pressure, the distillate contains methyl and ethyl iodides, and a mixture of ψ-thiopyrine and ethyl-ψ-thiopyrine. The methiodide of methylthiopyrine behaves similarly. *Ethyl-ψ-thiopyrine* (5-ethylthiol-1-phenyl-3-methylpyrazole), prepared by distilling methylthiopyrine at first under reduced pressure and then under the ordinary pressure, is a colourless oil boiling at 178° under 19—20 mm. and at 308—310° under 760 mm. pressure. The *methiodide* melts at 158°, and the *sulphone*, which crystallises in leaflets, at 61—62°. *isoPropyl-ψ-thiopyrine* (5-isopropylthiol-1-phenyl-3-methylpyrazole), prepared from the isopropiodide of thiopyrine, boils at 308—310° under 760 mm. pressure; the *methiodide* crystallises with H₂O, and when anhydrous melts at 170—171°; the *sulphone* forms needles melting at 83°. *isoButyl-ψ-thiopyrine* (5-isobutylthiol-1-phenyl-3-methylpyrazole) is an oil boiling at 313—314° under 760 mm. pressure; the corresponding *allyl* derivative is crystalline, melting at 56—57° and boiling at 184—188° under 11 mm. pressure; no *sulphone* was formed on oxidation.

Benzyl-ψ-thiopyrine (5-benzylthiol-1-phenyl-3-methylpyrazole) is obtained when the benzyl-chloride or -iodide of thiopyrine is distilled under the lowest possible pressure, and forms a colourless oil boiling at 246° under 20 mm. pressure; the *methiodide* is identical with the benzyliodide of thiopyrine. The *sulphone* forms colourless needles melting at 92°.

Methyl-ψ-thiopyrine (5-methylthiol-1-phenyl-3 : 4-dimethylpyrazole),



obtained by distilling either methylthiopyrine or the *methiodide*, forms plate-like, triclinic crystals melting at 56° and boiling at 179° under 15 mm. and at 310° under 760 mm. pressure. The methylthiol group is eliminated either by heating with hydrochloric acid or by reducing with sodium amalgam; with the first reagent, 1-phenyl-3 : 4-dimethylpyrazole (b. p. 277—278°) is formed, whilst in the latter case 1-phenyl-3 : 4-dimethylpyrazoline is produced. When treated with bromine, the methylthiol group is replaced by bromine, 5-bromo-1-phenyl-3 : 4-dimethylpyrazole being formed. The *hydrochloride* of methyl-ψ-thiopyrine crystallises in needles melting at 108°, and the *platinichloride* crystallises with 2H₂O in yellowish-red leaflets melting at 203°. The *sulphone* crystallises in needles melting at 137° and can be sublimed; its *methiodide* forms crystals melting at 188°, its *methochloride* melts at 81°, and the *platinichloride*, which crystallises in brown leaflets, melts and decomposes at 225°. On heating the *sulphone* with bromine under

pressure for five hours at 110° , 1-bromophenyl-3:4-dimethyl-5-methylsulphonepyrazole is formed, and crystallises in needles melting at 178° .

When the ethiodide of methylthiopyrine is distilled, methyl iodide is eliminated and 5-ethylthiol-1-phenyl-3:4-dimethylpyrazole produced; it is a viscid, colourless oil boiling at 180 — 185° under 15 mm. and at 316 — 318° under 760 mm. pressure. The sulphone forms needles melting at 115° . At the same time a small quantity of ethyl iodide is formed together with 5-thiomethylpyrazole, which separates as crystals.

K. J. P. O.

Condensation of *o*-Phenylenediamine with Phthalonic Acid.

CANULLO MANUELLI and G. SILVESTRI (*Gazzetta*, 1904, 34, i, 493—500).

—When heated either directly at 180 — 200° or in alcoholic solution in a reflux apparatus, a mixture of *o*-phenylenediamine and phthalonic

acid yields a quinoxaline derivative, $C_6H_4 \begin{smallmatrix} N:C \cdot C_6H_4 \cdot CO_2H \\ N:C \cdot OH \end{smallmatrix}$, which

crystallises from alcohol or ethyl acetate in shining, white laminæ, melting and decomposing at 232° , and is soluble in alkali solutions from which it is precipitated by mineral acids. By concentrated hydrochloric or 50 per cent. sulphuric acid it is partially dissolved, both the dissolved and insoluble portions becoming yellow with formation of an apparently tautomeric form, which is only stable in presence of strong acids, and is converted into the original compound by water. The barium salt (+ $10H_2O$) and the ammonium salt crystallise in white needles; the *o*-phenylenediamine salt crystallises from alcohol in pale yellow plates melting and decomposing at 203° . When heated either with acetic anhydride or with excess of acetic chloride as long as hydrogen chloride is evolved, the acid yields the corresponding lactone,

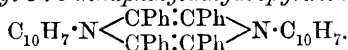
$C_6H_4 \begin{smallmatrix} N:C-C_6H_4 \\ N:C \cdot O \cdot CO \end{smallmatrix}$, which crystallises from alcohol in fan-shaped

aggregates of slender, white needles or from benzene in separate needles, gradually changing into prisms, and melts at 201 — 203° ; it dissolves in dilute potassium hydroxide solution and the benzene solution is fluorescent. With alcoholic ammonia, the lactone gives rise

to a derivative of pyridine, $C_6H_4 \begin{smallmatrix} N:C-C_6H_4 \\ N:C \cdot NH \cdot CO \end{smallmatrix}$, which crystallises from alcohol in slender, pale yellow needles melting at 266° . The corresponding platinichloride was prepared and analysed.

T. H. P.

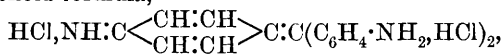
Condensations of Phenols and Aromatic Amines with Benzylideneaniline. CHARLES MAYER (*Compt. rend.*, 1904, 138, 1612—1613).—Benzylideneaniline condenses with α -naphthylamine in acetic acid solution to form a compound $C_{48}H_{84}N_2$, melting at 223° , crystallising in yellow, prismatic crystals, unchanged by boiling acid or alkali solutions, and giving no benzoyl derivative; it is probably 1:2:4:5-tetraphenyl-3:6-dinaphthylidihydropyrazine,



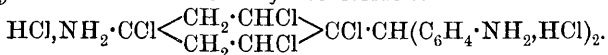
Benzylideneaniline condenses with α -naphthol to form a compound, $C_{30}H_{23}ON$, in the form of orange crystals melting at 158° , and identical with the 1:2:3-triphenyl-4:2- α -naphthoisoiazine obtained by Betti from the condensation of α -naphthol, benzaldehyde, and aniline (compare Abstr., 1901, i, 81, 611).

Benzylideneaniline forms with resorcinol a white, crystalline compound which becomes brick-red at 120° and deep green at 300° , and does not contain nitrogen. M. A. W.

Additive Hydrogen Chloride Compounds of Rosaniline Salts; their Dissociation, Thermo-chemistry, and Constitution. JULES SCHMIDLIN (*Compt. rend.*, 1904, 138, 1615—1617. Compare this vol., i, 698).—The formation of a white heptahydrochloride by the absorption of hydrogen chloride at the temperature of liquid air by the coloured trihydrochloride of rosaniline and its homologues is a reversible reaction, for if the white compound is sealed in a tube at the ordinary temperature, hydrogen chloride is evolved and the colour becomes successively yellow, orange, red, brown, and finally the black colour of the trihydrochloride, whilst the effect of heating the latter salt is to convert it into the monohydrochloride. From thermo-chemical considerations it appears that the first mol. of HCl absorbed by pararosaniline or by hexamethylpararosaniline trihydrochloride is in the form of a solution, the rest forming an integral part of the molecule, and the white compounds, which are the final products, and correspond with the absorption of 8 mols. of HCl, must be regarded as heptahydrochlorides holding 1 mol. of HCl in solution. Representing the coloured trihydrochloride by the quinonoid formula,



the formula suggested for the colourless heptahydrochloride or tetrachlorocyclohexanerosaniline trihydrochloride is



M. A. W.

Additive Compounds of Ammonia and Rosaniline. JULES SCHMIDLIN (*Compt. rend.*, 1904, 138, 1709—1711. Compare this vol., i, 698).—Prud'homme and Rabaut (compare Abstr., 1893, i, 640) have already observed that rosaniline salts absorb 2 mols. of dry ammonia to form a carmine-red compound; the author, however, finds that at -15° pararosaniline monohydrochloride absorbs 3.9 mols., and at -23° hexamethylpararosaniline monohydrochloride absorbs 4 mols. of ammonia to form colourless compounds, which in a vacuum give up the absorbed ammonia and revert to the original salts. In the case of pararosaniline monohydrochloride, the heat development accompanying the absorption of the first molecule of ammonia is 5.6 Cal., and of the second 4.9 Cal., the corresponding values for the hexamethylpararosaniline salt are 8.4 Cal. and 7.0 Cal. respectively. The author concludes that rosaniline salts are unsaturated compounds, capable of absorbing equivalent quantities of either acids or bases to form saturated colourless compounds, and, assuming the quinonoid formula,

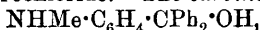
$C(C_6H_4 \cdot NH_2)_2 \cdot C \begin{smallmatrix} CH:CH \\ CH:CH \end{smallmatrix} > C:NH \cdot HCl$, for the unsaturated salt, the formula for the saturated ammonium compound would be $CH(C_6H_4 \cdot NH_2)_2 \cdot C(NH_2) \begin{smallmatrix} CH(NH_2) \cdot CH_2 \\ CH(NH_2) \cdot CH_2 \end{smallmatrix} > C(NH_2)_2 HCl$.

M. A. W.

Dibenzylideneacetone and Triphenylmethane. V. ADOLF BAEYER and VICTOR VILLIGER (*Ber.*, 1904, 37, 2848—2880. Compare *Abstr.*, 1902, i, 380, 769; 1903, i, 811; this vol., i, 308, 454).—The authors propose the name fuchsone for diphenylquinomethane (*Bis-trzycki* and *Herbst*, *Abstr.*, 1903, i, 639) as the basis of a general nomenclature. The phenylimine, $CPh_2 \cdot C \begin{smallmatrix} CH:CH \\ CH:CH \end{smallmatrix} > C:NPh$, is termed fuchsonophenylimine, its hydrochloride is fuchsonophenylimonium chloride, aurin is dihydroxyfuchsone, aniline blue, diphenylamino-fuchsonophenylimonium chloride, &c.

Condensation of benzophenone chloride with dimethylaniline in presence of zinc chloride leads to the formation of *p*-dimethylaminotriphenylcarbinol, which crystallises in sheaves of colourless needles and melts at 92—93°. With picric acid, it forms the insoluble red *picrate* of fuchsonedimethylimonium, which crystallises in prisms. The *oxalate*, $C_{21}H_{21}ON, C_2H_2O_4$, crystallises in white leaflets.

p-Methylaminotriphenylmethane, formed, along with a crystalline tertiary base, from methylaniline and benzhydrol, is best purified by conversion into its hydrochloride. The *carbinol*,



is obtained from the leuco-base by acetylation, oxidation with manganese dioxide and sulphuric acid, and hydrolysis of the *acetylmethylaminotriphenylcarbinol* formed. The *picrate* crystallises in orange-coloured leaflets or red needles.

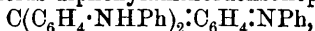
Diacetyl-p-diaminotriphenylmethane, obtained by heating *p*-diaminotriphenylmethane with acetic anhydride, crystallises in needles, melts at 233—234°, and is oxidised by manganese dioxide and sulphuric acid to *diacetyl-p-diaminotriphenylcarbinol*, which crystallises in red prisms, melts at 266—267°, and dissolves in concentrated sulphuric acid or warm glacial acetic acid to red solutions. The *carbinol*, obtained by hydrolysis of its diacetyl derivative, is best purified by conversion into its *picrate*, which crystallises in black prisms, and from that into its *methyl* ether, which crystallises in colourless plates and melts at 161—163°. When boiled with hydrochloric acid, the methyl ether yields *aminofuchsonium chloride*, $C_6H_4NH_2 \cdot CPh \cdot C_6H_4 \cdot NH_2Cl$, which forms yellowish-green crystals; the *nitrate* is yellowish-green, the *oxalate* is blue. *Di-p-aminotriphenylcarbinol*, obtained from the chloride by the action of barium carbonate in aqueous solution, crystallises in pointed prisms, melts, when slowly heated, at 167—168°, when rapidly heated from 160°, at 173—175°, decomposes immediately above its melting point, and commences to lose water on prolonged heating at 140°. *Aminofuchsonimine*, the base of Doebner's violet, is obtained by shaking its salts with sodium hydroxide, water, and benzene. The benzene solution closely resembles that of the colour-base

of magenta, but is more stable. After some days, it deposits an amorphous polymerisation product, which is also obtained from the carbinol on heating at 180° in a current of hydrogen, and which sinters above 250° .

p Phenylaminofuchsonphenylimine, the colour-base of viridine (compare Meldola, Trans., 1882, 41, 187), is formed when dianisylphenylcarbinol, aniline, and benzoic acid are heated together. It crystallises in brown, transparent plates and melts at 166 — 168° . The *picrate* crystallises in bronze, rhombic plates. The salts of *p*-phenylaminofuchsonphenylimoniums form green solutions; the chloride crystallises in needles; the sulphate crystallises in golden, rhombic plates or prisms, the *nitrate* in prisms.

The colour-base of magenta is soluble in water or dilute aqueous sodium hydroxide and may be extracted with benzene or ether; on adding more concentrated sodium hydroxide, the base is salted out. It combines easily with methyl alcohol to form the methyl ether of the carbinol, and with aniline to yield anilide, but more slowly with ethyl alcohol or water. The action of sodium hydroxide on paramagenta and of heat on the carbinol lead to the formation of substances which may be polymerisation products of the fuchsoneimine or the anhydride of the carbinol. By replacement of the methoxyl groups of tri-*p*-anisylcarbinol by aniline, a pure triphenylpararosaniline has been obtained. This gives a characteristic, insoluble, crystalline *picrate*. Diphenylamine-blue probably contains triphenylpararosaniline, commercial triphenylpararosaniline-blue gives no trace of the *picrate*.

Diphenylaminofuchsonphenylimonium benzoate is formed when tri-*p*-anisylcarbinol is heated with aniline and benzoic acid. It crystallises in small, blue, transparent leaflets, and, when shaken with aqueous sodium hydroxide, yields diphenylaminofuchsonphenylimine,



which crystallises in plates and melts at 237 — 238° . It combines readily with aniline in pyridine, or with methyl alcohol, more slowly with ethyl alcohol or methylaniline; the alkyl ethers and anilides so formed are obtained as syrups. The colour-base is reduced to the leuco-base; with acids it forms the salts of triphenylpararosaniline (diphenylaminofuchsonphenylimonium salts). The *chloride* crystallises in stellate clusters of needles; the *picrate* mentioned above crystallises in glistening, bronze leaflets. The action of water on the colour-base in presence of a trace of an acid leads to the formation of the carbinol (triphenylpararosaniline), which crystallises with benzene of crystallisation and melts at 85° . *Triphenylparaleucaniline* crystallises in glistening needles and melts at 182 — 184° .

The action of sodium methoxide on pararosaniline in methyl-alcoholic solution leads to the formation of the *methyl ether* of triaminotriphenylcarbinol (Fischer, Abstr., 1901, i, 82). It crystallises in rhombic leaflets containing 1 mol. of ether of crystallisation, sinters, and loses ether at 105° . At 110° , the ether commences to decompose with the loss of methyl alcohol.

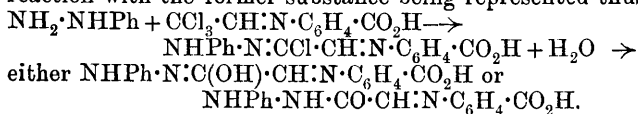
The *methyl ether* of triaminotritolylcarbinol crystallises in long leaflets and melts and decomposes at 178° . The *methyl ether* of hexamethyltriaminotriphenylcarbinol is formed by the action of sodium

methoxide on crystal-violet. It crystallises in rhombic plates and melts at 159—160° when heated in a closed capillary.

Whilst the monoaminotriphenylcarbinols do not crystallise, but form stable crystalline carbinol salts, the di- and tri-amino-compounds are crystalline, and form unstable carbinol salts (not yet isolated), but stable crystalline fuchsonium salts.

Fuchsonimine has not been isolated, as, on formation, it immediately polymerises, or, in presence of water, forms the carbinol. In benzene solution, monoaminofuchsonimine polymerises slowly, the diamino-compound still more so; the increase of the amino-groups is accompanied by increase in the stability of the dye salts and of their usefulness as dyes. G. Y.

Chloralamino-compounds. I. S. GÄRTNER (*Annalen*, 1904, 332, 226—245).—The interaction of trichloroethylideneanthranilic acid with phenylhydrazine and semicarbazide has been studied, the reaction with the former substance being represented thus:



Semicarbazide reacts in a similar manner.

The *monophenylhydrazide* of 2-carboxyphenyliminoacetic acid separates from a solution of trichloroethylideneanthranilic acid in alcohol, to which an aqueous solution of phenylhydrazine sulphate has been added, and forms pale yellow prisms melting and decomposing at 243°; it is soluble in the equivalent quantity of a solution of sodium carbonate or sodium hydroxide, with an intense yellow coloration; on addition of excess of alkali, the salt separates; the *potassium* salt, $\text{C}_{15}\text{H}_{13}\text{O}_3\text{N}_3\text{K}$, crystallises in yellow needles, the *calcium* salt in needles with $8\frac{1}{2}\text{H}_2\text{O}$; the *barium* salt is anhydrous. The compound is only hydrolysed after prolonged boiling with a large excess of alkali hydroxide. The *ethyl* ester, prepared from the silver salt and ethyl iodide, crystallises in white needles or yellow prisms melting at 140—141°, and the *acetyl* compound in needles melting at 268°. When the acetyl derivative is

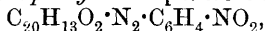
heated under reduced pressure, the *anhydride*, $\text{C}_6\text{H}_4 \begin{array}{c} \text{N} : \text{CH} \cdot \text{CO} \\ \text{CO} - \text{N} \cdot \text{NPhAc} \end{array}$, is obtained as yellow needles melting at 260—262°, and is decomposed when heated under the ordinary pressure, yielding acetanilide. If the anhydride is warmed with dilute sodium hydroxide, the acetyl group is removed, water added, and the original phenylhydrazide regenerated, together with a neutral compound which melts at 170° and gives a green coloration with sulphuric acid.

When oxidised with dilute nitric acid, the phenylhydrazide yields *p*-nitrosalicyclic acid, oxalic acid, and traces of benzoic acid. If permanganate is used instead of nitric acid, oxalyanthranilic acid is produced (melting and decomposing at 210°); the *silver* salt was analysed.

The *semicarbazide* of 2-carboxyphenyliminoacetic acid,
 $\text{NH}_2 \cdot \text{CO} \cdot \text{N}_2\text{H}_4 \cdot \text{CO} \cdot \text{CH} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H},$

prepared from semicarbazide hydrochloride and trichloroethylidene-anthranilic acid, crystallises in needles decomposing at 278—280°; the calcium salt (with 11H₂O) and the barium salt (with 9½H₂O) crystallise in long needles.
K. J. P. O.

Azo-dyes from 3:3'-Dihydroxy-2:2'-dinaphthyl. M. EMMANUEL Pozzi-Escot (*Compt. rend.*, 1904, 138, 1618—1619).—3:3'-*Dihydroxy-2:2'-dinaphthyl-1:1'-disazo-β-naphthalene*, C₂₀H₁₀(OH)₂(N₂·C₁₀H₇)₂, obtained by the action of 2 mols. of diazotised β-naphthylamine on 1 mol. of 3:3'-dihydroxy-2:2'-dinaphthyl, has a bright red colour, is insoluble in water, soluble in alcohol forming a bright carmine-red solution, and soluble in sulphuric acid with a blue colour. 3:3'-*Dihydroxy-2:2'-dinaphthyl-1-azo-β-naphthalene*, C₂₀H₁₃O₂·N₂·C₁₀H₇, prepared from 1 mol. of diazotised β-naphthylamine and 1 mol. of 3:3'-dihydroxy-2:2'-dinaphthyl, has a violet colour, is insoluble in water, forms a violet solution in sulphuric acid, and its sulphonic derivative is soluble in water and dyes wool a reddish-brown. 3:3'-*Dihydroxy-2:2'-dinaphthyl-1-azo-p-nitrobenzene*,

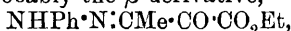


has a red colour, is very slightly soluble in water, and forms a brown solution in sulphuric acid. 3:3'-*Dihydroxy-2:2'-dinaphthyl-1:1'-disazo-p-nitrobenzene* has an orange colour, is very slightly soluble in water, but the solution colours wool a bright orange; it forms a brown solution in sulphuric acid. 3:3'-*Dihydroxy-2:2'-dinaphthyl-1:1'-disazodiphenyl*,

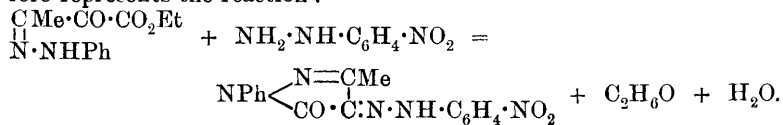
$\text{OH}\cdot\text{C}_{10}\text{H}_5\cdot\text{N}_2\cdot\text{C}_6\text{H}_4$, $\text{OH}\cdot\text{C}_{10}\text{H}_5\cdot\text{N}_2\cdot\text{C}_6\text{H}_4$, has a brown colour, is insoluble in water, and forms a greyish-green solution in sulphuric acid. 3:3'-*Dihydroxy-2:2'-dinaphthyl-1-azoanisole* is brown, insoluble in water, and soluble in nitric acid. The existence of azo-derivatives of β-dinaphthol points to the linking of the two naphthalene rings being in the 2:2'- and not the 1:1'-position, as hitherto assumed.

M. A. W.

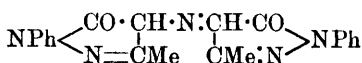
Reactions of αβ-Diketobutyric Esters. I. Action of Phenylhydrazine. LOUIS BOUVEAULT and ANDRÉ WAHL (*Compt. rend.*, 1904, 139, 134—136. Compare this vol., i, 556).—Ethyl diketobutyrate-phenylhydrazone is probably the β-derivative,



for it reacts with *p*-nitrophenylhydrazine to form 4-*p*-nitrobenzeneazo-1-phenyl-3-methyl-5-pyrazolone identical with the compound prepared by Bülow by the action of phenylhydrazine on ethyl *p*-nitrobenzene-azoacetoacetate (compare Abstr., 1899, i, 271), in which the phenylhydrazone grouping is in the β-position; the following equation therefore represents the reaction:

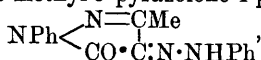


Further, on boiling an acetic acid solution of the ethyldiketobutyratephenylhydrazone, it is converted into rubazonic acid,



(compare Knorr, Abstr., 1887, 602).

By the action of phenylhydrazine on ethyl diketobutyrate at a high temperature, 1-phenyl-3-methyl-5-pyrazolone-4-phenylhydrazone,



is obtained, identical with the compound obtained by Knorr, (1) by the action of diazobenzene chloride on phenylmethylpyrazolone (compare Abstr., 1887, 602); (2) by boiling rubazonic acid and phenylhydrazine in acetic acid solution (compare Abstr., 1888, 724); and by Japp and Klingemann by the action of phenylhydrazine on ethyl phenylhydrazoneacetoglyoxylate (compare Trans., 1888, 53, 530).

M. A. W.

Compounds of Albumin with Bismuth and Formaldehyde.

KALLE & Co. (D.R.-P. 150201).—Bismuthose, prepared by adding egg-albumin to a solution of bismuth nitrate and sodium chloride (compare D.R.-P. 117269), swells to a gelatinous mass with water. This property is destroyed when formaldehyde is added. The product is washed until neutral, pressed, and dried. Hot dilute acids or alkalis hydrolyse it, setting free formaldehyde.

C. H. D.

Combinations of Mucoids with other Proteids. E. R. POSNER

and WILLIAM J. GIES (*Amer. J. Physiol.*, 1904, 11, 404—436).—Addition of a solution of a mucoid to that of another proteid causes the formation of a precipitate, which is stated to be a compound and not a mixture of the mucoid and proteid. The glucothionic acid in mucoid is believed to be concerned in the reaction.

W. D. H.

The Carbohydrate Group in Proteids. LEO LANGSTEIN (*Zeit. physiol. Chem.*, 1904, 42, 171—174).—Polemical. The results recorded by Abderhalden, Bergell, and Dorpinghaus (this vol., i, 640) are not new, but merely confirmatory of work previously published by others, including the author.

W. D. H.

Carbohydrates from Serum Globulins. II. LEO LANGSTEIN (*Monatsh.*, 1904, 25, 453—463. Compare Abstr., 1902, i, 66; 1903, i, 374, 734).—When boiled with water (Mörner, Abstr., 1894, i, 352), with dilute alkali hydroxides, or with baryta solution, serum globulin yields a polysaccharide, which contains nitrogen and resembles Fränkel's albumin (Abstr., 1899, i, 396), but does not give Ehrlich's reaction with dimethylaminobenzaldehyde. When boiled with 2.2 per cent. hydrochloric acid, it yields glucosamine. The dextrose of globulin is not a component of the albumin molecule, but is probably in molecular combination, the stability being equal to that of the water of crystallisation of salts.

G. Y.

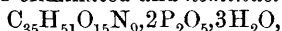
The Amount of Sulphur in the Digestion Products of Casein.

WACŁAW VON MORACZEWSKI (*Beitr. chem. Physiol. Path.*, 1904, 5, 489—499).—The amount of sulphur in paranuclein is constant, and

independent of the time of the digestion with pepsin-hydrochloric acid. During digestion, a part of the sulphur of the casein is lost, and this amount increases with the intensity of the digestive process.

W. D. H.

Nucleic Acid. CARL LUCA ALSBERG (*Chem. Centr.*, 1904, ii, 133—134; from *Arch. exp. Path. Pharm.*, 51, 239—247).—Nucleic acid, prepared from the semen of the turbot, *Lota vulgaris*, is identical with the acid obtained from salmon milt. By digesting copper nucleate with a 2 per cent. solution of sulphuric acid for 8—10 days at 38—40°, 1 mol. of purine base is eliminated and *heminucleic acid*,



is obtained. This acid is distinguished from nucleic acid by the fact that solutions of its alkali salts in dilute acetic acid are not precipitated by hydrochloric acid or cupric chloride. Experiments on the action of acids on nucleic acid confirmed Schmiedeberg's results (*Abstr.*, 1900, i, 267); the acid loses a portion of the purine bases with ease, but the rest only with difficulty, whilst the nucleotin is uniformly decomposed. The barium compound of a substance $\text{C}_{47}\text{H}_{81}\text{O}_{30}\text{N}_9, 2\text{P}_2\text{O}_5$, prepared by boiling copper nucleate for 24 hours with a saturated solution of baryta water, was found to consist of a mixture of hemi-nucleic acid and a compound $\text{C}_{12}\text{H}_{30}\text{O}_{15}$. A small quantity of the barium salt of nucleotin, $\text{Ba}_4\text{C}_{30}\text{H}_{34}\text{O}_{13}\text{N}_4, 11\text{H}_2\text{O}$, has been obtained by heating copper nucleate with baryta water in superheated steam.

E. W. W.

Epinephrine (Adrenaline). EMIL ABDERHALDEN and PETER BERGELL (*Ber.*, 1904, 37, 2022—2024).—Epinephrine is very liable to oxidation during the course of separation and purification. By purifying in an atmosphere of hydrogen, a substance was obtained which gave analytical values corresponding with the formula $\text{C}_9\text{H}_{13}\text{O}_3\text{N}$ suggested by Pauly. Abel's formula, $\text{C}_{10}\text{H}_{13}\text{O}_3\text{N}, \frac{1}{2}\text{H}_2\text{O}$, appears to have been based on the analysis of a partially-oxidised product containing a low percentage of carbon and hydrogen.

T. M. L.

Products of Distillation of Hæmatin with Zinc Dust. J. A. MILROY (*Proc. Physiol. Soc.*, 1904, xxiv—xxvi; *J. Physiol.*, 31).—At least three volatile substances are obtained by the distillation of hæmatin with zinc dust, two resembling in their spectroscopic appearances hæmatoporphyrin and urobilin, although differing from the latter in regard to solubility, and one probably allied to the hæmopyrrole obtained by Nencki and Zaleski.

W. D. H.

β -Hæmin. KARL A. H. MORNER (*Zeit. physiol. Chem.*, 1904, 41, 542—547).—The author agrees with Küster's conclusion (this vol., i, 357) that there is only one hæmin, and that β -hæmin, acetohæmin, and hæmin are identical. It is suggested that β -hæmin may contain a small amount of an ethereal derivative of hæmin.

J. J. S.

Function of Peroxides in the Living Cell. IX. Rate of the Peroxydase Reaction. ALEXIS BACH and ROBERT CHODAT (*Ber.*, 1904, 37, 2434—2440. Compare this vol., i, 542).—It had previously been shown that, during the oxidation of pyrogallol, the peroxydase used and hydrogen peroxide react in definite proportions. The rate of the action of the peroxydase on hydrogen peroxide has now been measured, the amount of oxygen liberated being measured by its action on hydriodic acid. The rate at which the peroxydase disappears increases with the concentration of the peroxydase, but more quickly than the latter concentration increases. In the reaction between hydriodic acid and hydrogen peroxide in the presence of the peroxydase, the latter possesses a much greater power of rendering the hydrogen peroxide active than it does during the oxidation of pyrogallol.

The rate of the peroxydase reaction follows the Law of Mass Action, when the reaction is not destroyed by the presence of by-products.

The peroxydase is considered to be a ferment, although it gradually disappears during the oxidation. A. McK.

Inhibitory Influence of Foreign Molecules on the Action of Histozyms, and Ferments on Amides and Glucosides. MAX GONNERMANN (*Pflüger's Archiv*, 1904, 103, 225—256. Compare Abstr., 1903, i, 590).—The action of emulsin on glucosides and of extracts of animal organs on amides and glucosides was investigated in the presence of inhibitory agents such as ammonium sulphate, potassium chloride, quinine, &c. Differences in the amount and rate of inhibition are noted. W. D. H.

Conversion of Nitrobenzene into Aniline by means of Philothion and Yeast Reductases. M. EMMANUEL POZZI-ESCOT (*Chem. Centr.*, 1904, i, 1646—1647; from *Bull. Assoc. Chem. Sucr. Dist.*, 21, 1073—1075. Compare Abstr., 1903, i, 670, and Abelous and Gérard Abstr., 1900, ii, 226).—The following experiment shows that nitrobenzene may be reduced to aniline by the action of philothion on reducing diastases. Beer or wine yeast which has been pressed, but not dried, is mixed with alcohol and water, and after remaining 30—40 hours the mixture is filtered and a few drops of nitrobenzene added to the filtrate. The odour of nitrobenzene disappears in 24 hours. The presence of aniline cannot be detected directly, however, by the ordinary methods, but after neutralising with hydrochloric acid and removing the alcohol by distillation the characteristic reactions of the base are readily obtained. E. W. W.

Organic Chemistry.

Sodium Derivatives of Acetylene. M. SKOSAREWSKY (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 863—872).—The sodium derivatives of acetylene were first prepared by Berthelot (*Ann. Chim. Phys.*, 1866, [iv], 9, 385), who ascribed to them the formulæ C_2Na_2 and C_2HNa . Later, however, Moissan (*Abstr.*, 1898, ii, 332, and 1899, i, 241) suggested that the mono-sodium derivative of acetylene is more accurately represented by the formula C_2Na_2, C_2H_2 . The results of the author's experiments show, on the other hand, that all the known facts concerning this compound are explained by the composition $CH:CNa$, and that the sodium derivatives of mono-substituted acetylenes are represented by $CR:CNa$.

The action of iodine on the mono-sodium derivative of acetylene gives rise to the compound C_2HI_3 in the following manner: (1) $CH:CNa + I_2 = CH:CI + NaI$, and (2) $CH:CI + I_2 = CHI:CI_2$. If the formula of the sodium derivative were C_2Na_2, C_2H_2 , the action of iodine should yield $C_2H_2I_4$.

Further, when heated in an atmosphere of carbon dioxide, this sodium derivative yields exclusively the compound $CH:C\cdot CO_2Na$, and not $CO_2Na\cdot C\dot{H}\cdot CO_2Na$ or $CNa\dot{C}\cdot CO_2Na$, as should be the case if the formula C_2Na_2, C_2H_2 were the correct one. T. H. P.

Action of Nitrogen Peroxide on Diallyl. K. W. SIDORENKO (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 898—905).—On passing nitrogen peroxide (approx. $2NO_2$) into an ethereal solution of diallyl (1 mol.) kept cool by snow and salt, and reducing the product obtained by means of tin and hydrochloric acid, an unsaturated amine, $C_6H_{10}(NH_2)_2$, is obtained, the *platinichloride*, *hydrochloride*, and *oxalate* of which were prepared and analysed; the last-named salt melts and decomposes at 166° if slowly heated, and at about 190° if rapidly heated. The structure of the amine is probably



Slow Oxidation of Cyanogen and of Cyanides by Free Oxygen. MARCELLIN BERTHELOT (*Compt. rend.*, 1904, 139, 169—177).—The author has investigated the action of oxygen on aqueous and alcoholic solutions of potassium cyanide, hydrogen cyanide, and cyanogen, the influence of light on the change being also examined. The solutions were in most cases in contact with mercury, and at the end of the experiment were examined for the presence of the metal.

Aqueous or alcoholic potassium cyanide slowly absorbs oxygen; the rate of absorption increases with rise of temperature, and is greater in sunlight than in the dark. In presence of mercury, the metal dissolves, especially when the system is insulated. An aqueous solution of hydrocyanic acid also absorbs oxygen, although to a much smaller extent.

Aqueous or alcoholic solutions of cyanogen take up oxygen, and the cyanogen soon disappears, carbon dioxide being produced, and in presence of mercury traces of the metal are dissolved, the action being accelerated by light.

Further experiments with aqueous cyanogen solutions containing potassium cyanide or hydrogen cyanide gave similar results. In the case of an alcoholic solution containing cyanogen and potassium cyanide, the absorption of oxygen, whether in sunlight or in the dark, is not accompanied by solution of mercury.

A solution of potassium hydroxide in absolute alcohol also absorbs oxygen in sunlight, but mercury is not dissolved. H. M. D.

Changes in the Composition of some Ferrocyanides of Cadmium and Zinc after Precipitation. EDMUND H. MILLER and M. J. FALK (*J. Amer. Chem. Soc.*, 1904, 26, 952—959. Compare Abstr., 1902, i, 429).—On adding a slight excess of potassium ferrocyanide to a dilute solution of cadmium chloride containing ammonium chloride at 50—100°, a crystalline precipitate having the composition $\text{Cd}(\text{NH}_4)_2\text{Fe}(\text{CN})_6$ is obtained (compare Waring, this vol., ii, 211); when, however, the cadmium chloride is added to an excess of potassium ferrocyanide either at 50° or at 100°, a mixture having the composition $3\text{CdK}_2\text{Fe}(\text{CN})_6, 7\text{Cd}(\text{NH}_4)_2\text{Fe}(\text{CN})_6$ is precipitated.

When cadmium potassium ferrocyanide, $\text{CdK}_2\text{Fe}(\text{CN})_6$, is agitated with dilute ammonia at 50° for a week, it is transformed into a mixture of $6\text{Cd}_2\text{Fe}(\text{CN})_6, 3\text{Cd}(\text{NH}_4)_2\text{Fe}(\text{CN})_6$ and $\text{CdK}_2\text{Fe}(\text{CN})_6$; with ammonium chloride under similar conditions, a larger proportion of normal cadmium ferrocyanide is formed, the product having the composition $3\text{Cd}_2\text{Fe}(\text{CN})_6, 6\text{Cd}(\text{NH}_4)_2\text{Fe}(\text{CN})_6, \text{CdK}_2\text{Fe}(\text{CN})_6$.

Cadmium ammonium ferrocyanide, $\text{Cd}(\text{NH}_4)_2\text{Fe}(\text{CN})_6$, is similarly transformed by dilute aqueous potassium hydroxide into a mixture having the same composition as that formed when cadmium chloride is precipitated with an excess of potassium ferrocyanide, namely, $3\text{CdK}_2\text{Fe}(\text{CN})_6, 7\text{Cd}(\text{NH}_4)_2\text{Fe}(\text{CN})_6$. Application is made of these facts to the theory of the cadmium precipitation.

The precipitate obtained by adding potassium ferrocyanide to a solution of zinc chloride containing ammonium chloride at 60° has the composition $\text{Zn}_{15}(\text{NH}_4)_8\text{K}_2[\text{Fe}(\text{CN})_6]_{10}$. This complex salt is transformed by agitation with potassium chloride at 70° into the simpler mixture $\text{Zn}_2\text{Fe}(\text{CN})_6, \text{K}_2\text{Fe}(\text{CN})_6$, the ferrocyanide obtained in the precipitation of zinc when no ammonium chloride is present; conversely, the latter mixture is transformed into the former by agitation with ammonium chloride. The bearing of these facts on the titration of zinc by potassium ferrocyanide is discussed. W. A. D.

Preparation of Trichloroisopropyl Alcohol. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 151545).—Trichloroisopropyl alcohol, $\text{CCl}_3\cdot\text{CHMe}\cdot\text{OH}$ (Thurnlackh, Abstr., 1882, 295), may be prepared by adding magnesium methyl iodide or magnesium methyl bromide to a cooled solution of chloral in dry ether, acidifying and distilling. It melts at 49.2° and has hypnotic properties (compare this vol., i, 279). C. H. D.

Oxooctenol. N. PRILESCHAEFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 872—881).—The reduction of oxooctenol in ethyl-alcoholic solution by means of sodium yields a *glycol*, $C_8H_{18}O_2$, which crystallises from light petroleum in well-formed prisms, melts at $64.5-65^\circ$, is very volatile, and has a pleasant camphoraceous odour. On oxidation with 1 per cent. potassium permanganate solution, it gives oxooctenol. No intermediate compound resembling this glycol or giving oxooctenol on oxidation could be found among the products obtained by oxidising isobutylene, which is the method of preparing oxooctenol (Butleroff, *Abstr.*, 1882, 936).

Oxooctenol does not react with hydroxylamine, hydrazine hydrate, semicarbazide, *p*-bromophenylhydrazine, or phenylhydrazine. When dehydrated by distilling with anhydrous oxalic acid, it yields an unsaturated *ketone*, $C_8H_{14}O$, which boils at $137-139^\circ$ under 754 mm. pressure, readily decolorises permanganate solution and absorbs bromine (2 atoms), and gives a *carbazone*, $C_9H_{18}ON_3$, melting at $151.5-152.5^\circ$. The products of the oxidation of this ketone by permanganate are acetic, trimethylacetic, and formic acids. These results would indicate a hydroxy-ketonic structure for oxooctenol, but as the above dehydration takes place in a strongly acid liquid, it is probable that isomeric change takes place, inasmuch as oxooctenol does not react with the ordinary reagents for the carbonyl group.

Besides the glycol referred to above, the products of the reduction of oxooctenol by sodium ethoxide comprise also a *hydroxy-ketone*, $CM_3 \cdot CO \cdot CM_2 \cdot OH$, which is isomeric with oxooctenol and yields a *semicarbazone*, $C_9H_{19}O_2N_3$, crystallising from alcohol in feathery, drusy masses, melting at $185.5-186.5^\circ$. This action of alkalis on oxooctenol must be regarded, not as an isomeric change, but as simultaneous reduction and oxidation, similar to the action of alkalis on aldehydes.

The above facts show clearly that oxooctenol is not to be regarded as the first product of the oxidation of an oxide previously formed from isobutylene, as was suggested by Butleroff (*loc. cit.*). T. H. P.

Preparation of Acetyl Chloride. ALFRED WOHL (D.R.-P. 151864).—The reaction between calcium acetate and sulphuryl chloride is generally very incomplete, but may be rendered almost complete by prolonged mixing of the reacting compounds in a ball mill. A double compound is first formed from the sulphuryl chloride and a part of the calcium acetate, which gives up no acetyl chloride to benzene or on heating, and decomposition into acetyl chloride and calcium sulphate only occurs after prolonged mechanical mixing. C. H. D.

Preparation of Nitroacetic Esters. LOUIS BOUEVAULT and ANDRÉ WAHL (*Bull. Soc. chim.*, 1904, [iii], 31, 847—854).—The methods previously described by Franchimont (*Abstr.*, 1889, 1143) and the authors (*Abstr.*, 1901, i, 5 and 445) for the preparation of these esters do not give satisfactory yields. The following process is now recommended: ethyl acetoacetate (50 grams) is dissolved in acetic anhydride (25 grams) and the liquid, previously warmed to 35° , is thoroughly agitated by means of a current of air, while a mixture of

anhydrous nitric acid (27 grams) with cold acetic anhydride (27 grams) is added, drop by drop, from a bromine tube dipping into the liquid, the temperature being maintained at 32—34°. The mixture is then thrown into water, and from the precipitated oil, which also contains ethyl bisanhydronitroacetate and dinitroacetate (Bouveault and Bongert, Abstr., 1901, i, 579), ethyl nitroacetate is isolated by solution in ether and extraction with an aqueous solution of sodium hydroxide.

Methyl nitroacetate, similarly prepared, boils at 94—95° under 16 mm. pressure and is slightly soluble in water (compare Wieland, Abstr. 1903, i, 769). *iso*Butyl nitroacetate is a colourless liquid, which distils at 102° under 8 mm. pressure and furnishes a colourless, crystalline *potassium* salt. With this ester is produced a small quantity of *isobutyl* diketobutyrate (this vol., i, 557). T. A. H.

Dissimilarity in the Reactions of *d*- and *l*-Lactic Acids. EMILE JUNGLEISCH (*Compt. rend.*, 1904, 139, 203—206).—Solutions of quinine *d*-lactate or quinine *l*-lactate were precipitated with the hydroxide of barium, calcium, or potassium, the quinine removed by ether or amyl alcohol, and the rotatory power of the metallic lactate in solution, as well as that of the zinc lactate obtained by double decomposition, was measured. The rotatory power of the solution obtained from the *d*-lactate differed in every case from that of the solution obtained from the *l*-lactate. Using calcium hydroxide to precipitate the quinine, the solutions from the *d*- and *l*-lactates gave respectively for α_D -1.5° and +0.5°. These facts indicate that the *d*- and *l*-lactic acids differ considerably in their behaviour; both undergo racemisation, but the *l*-acid is more readily transformed (compare this vol., i, 645).

H. M. D.

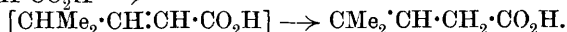
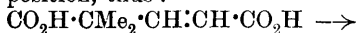
Pyruvic Acid as a Decomposition Product of Proteids. KARL A. H. MÖRNER (*Zeit. physiol. Chem.*, 1904, 42, 121—131. Compare Suter, Abstr., 1895, i, 691).—Horn, human hair, and blood serum all yield small amounts of pyruvic acid when heated at 90° with dilute hydrochloric acid. The acid was characterised by conversion into its phenylhydrazone, which melts at 180—182°. Casein yields a mixture of acids which with phenylhydrazine gives a mixture of phenylhydrazones melting at about 150° and probably derived from pyruvic acid and the homologous propionylformic acid.

It is not probable that pyruvic acid stands in any simple relationship to cystin.

J. J. S.

Vinyldimethylacetic Acid. EDMOND E. BLAISE and A. COURTOT (*Compt. rend.*, 1904, 139, 292—294).—The acid obtained by boiling an aqueous solution of sodium β -iodo- $\alpha\alpha$ -dimethylglutarate (compare Abstr., 1903, i, 604) or by distilling $\alpha\alpha$ -dimethylglutaconic acid (compare Perkin, Trans., 1902, 81, 256) is not dimethylvinylacetic acid, as stated by Perkin, but the isomeric pyroterebic acid, with which it has been identified by means of its boiling point, its anilide, its calcium salt, and its conversion into *isocapro*lactone by the action of sulphuric acid (compare Blanc, this vol., i, 647). The formation of pyroterebic acid from $\alpha\alpha$ -dimethylglutaconic acid involves therefore the elimination of carbon dioxide from the carboxyl group in the α -position

and the migration of the ethylenic linking from the $\beta\gamma$ - to the $\alpha\beta$ -position, thus :



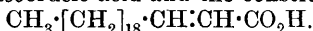
Bouveault's *aa*-dimethylisocrotonic acid (compare Abstr., 1900, i, 131) is identical with dimethylvinylacetic acid, since it yields dimethylmalonic acid on oxidation with potassium permanganate. It crystallises at a low temperature and does not yield a lactone on treatment with sulphuric acid.

M. A. W.

Action of Potassium Nitrite on Ethyl Mucobromate. HENRY B. HILL and OTIS F. BLACK (*Amer. Chem. J.*, 1904, 32, 228—242).—Ethyl mucobromate, $\text{CHO}\cdot\text{CBr}\cdot\text{CBr}\cdot\text{CO}_2\text{Et}$, reacts with potassium nitrite in dilute alcoholic solution, forming *potassium ethyl nitromaleate*, $\text{CO}_2\text{Et}\cdot\text{C}(\text{NO}_2)\cdot\text{CH}\cdot\text{CO}_2\text{K}$, crystallising in colourless prisms. The *methyl* ester, from methyl mucobromate, is similar. Both esters are oxidised by bromine and water to dibromonitromethane and glyoxylic acid. Ammonia forms a mixture of the potassium and ammonium salts of *nitromaleamic acid*, $\text{NH}_2\cdot\text{CO}\cdot\text{C}(\text{NO}_2)\cdot\text{CH}\cdot\text{CO}_2\text{H}$, which decomposes on evaporation, but forms stable *potassium*, *ammonium*, and *silver* salts. Barium hydroxide reacts with potassium ethyl nitromaleate to form a basic barium nitromaleate, which is decomposed by hydrochloric acid, forming β -nitrolactic acid (β -nitro- α -hydroxypropionic acid), $\text{NO}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$, which crystallises from ether or chloroform in small, white prisms and melts at 76 — 77° (uncorr.). It dissolves readily in water, alcohol, or ether, more sparingly in chloroform. By crystallising its strychnine salt and decomposing with hydrochloric acid, a levorotatory modification is obtained. The *barium*, *calcium*, and *silver* salts are described. The *acetyl* derivative crystallises from ether and chloroform in large, white octahedra, melts at 90 — 91° , and dissolves readily in water. Tin and hydrochloric acid reduce nitrolactic acid to *isoserin* (β -amino- α -hydroxypropionic acid).

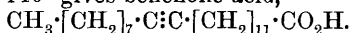
C. H. D.

isoErucic Acid. GIACOMO PONZIO (*Gazzetta*, 1904, 34, ii, 50—55).—By adding hydrogen iodide to erucic acid and afterwards removing it by means of alcoholic potassium hydroxide, Alexandroff and Saytzeff (Abstr., 1893, i, 549) obtained an acid melting at 54 — 56° to which they gave the name *isoerucic acid* and the constitution



The authors have prepared this acid and studied its transformations, from which they find that it has the same structure as erucic acid, namely, $\text{CH}_3\cdot[\text{CH}_2]_7\cdot\text{CH}\cdot\text{CH}\cdot[\text{CH}_2]_{11}\cdot\text{CO}_2\text{H}$, so that Alexandroff and Saytzeff's statement (*loc. cit.*) that these two acids are structural isomerides is inaccurate.

The action of bromine in acetic acid solution on *isoerucic acid* yields dibromobehenic acid, which, when treated with alcoholic potassium hydroxide at 130 — 140° gives behenolic acid,



When heated with nitric acid of sp. gr. 1.4, *isoerucic acid* is transformed into nonylic and brassilic acids together with a small quantity of dinitrononane.

T. H. P.

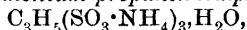
Resolution of Racemic Acid by means of *Aspergillus Niger*. SEBASTIANO CONDELLI (*Gazzetta*, 1904, 34, ii, 86—96. Compare Ulpiani and Condelli, *Abstr.*, 1900, ii, 493).—The optimum temperature for the decomposition of racemic acid by *Aspergillus niger* is about 35°. Both the isomerides undergo further decomposition, the *d*-tartaric acid formed being destroyed more at low temperatures, and the *l*-acid at the higher temperatures. Probably the *l*-acid becomes transformed into the *d*-form, which is readily attacked. T. H. P.

Action of some Fatty Acids on Starch. A. G. KLDIASCHWILI (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 905—908).—The direct action of formic acid on starch yields the monoformyl derivative of this carbohydrate, to which, on the basis of cryoscopic measurements in chloroacetic acid and phenol, the formula $(C_7H_{10}O_6)_6$ or $(C_7H_{10}O_6)_6 \cdot H_2O$ is ascribed. The author is not convinced of the chemical individuality of the compound owing to the possibility of the presence of the corresponding ethers of various dextrans, but it is shown that the ether of ordinary dextrin is not present. Analogous compounds are obtained by the action of mono-, di-, and tri-chloroacetic acids on starch. The mono- and di-chloro-compounds dissolve readily in acetone, and have been obtained pure. The amount of acid in these ethers shows them to be mono-acyl compounds. With iodine, these compounds give no characteristic coloration, but, after hydrolysis with potassium hydroxide, the monochloro-derivative gives a dextrin coloration with iodine, whilst the dichloro-compound yields no coloration, and the trichloro-ether only an indefinite one. T. H. P.

Theory of the Process of Saponification. LUIGI BALBIANO (*Gazzetta*, 1904, 34, ii, 55—56).—The author replies to the criticisms of Lewkowitsch (*Abstr.*, this vol., i, 6 and 283. Compare Balbiano, *Abstr.*, 1903, i, 547). T. H. P.

Propanetrisulphonic Acid. WILLIAM B. SCHÖBER (*Amer. Chem. J.*, 1904, 32, 165—167).—The only derivatives of propanetrisulphonic acid hitherto described are the barium salts prepared by Schaufelin (*Annalen*, 1868, 148, 117).

When $\alpha\beta\gamma$ -tribromopropane (tribromohydrin) is heated with ammonium sulphite, ammonium propanetrisulphonate,



is obtained. The barium salt crystallises with $5H_2O$.

E. G.

Reactions of the Hexoses. RUDOLF OFNER (*Monatsh.*, 1904, 25, 611—620).—Seliwanoff's reaction (*Abstr.*, 1887, 459) takes place with aldoses as well as ketoses, if the concentration of the hydrochloric acid is favourable. If used as a reaction for ketoses, the hydrochloric acid must not be stronger than 12 per cent. Contrary to Neuberg's statement (*Abstr.*, 1902, i, 264), osazones are formed by the interaction of secondary asymmetric hydrazines and aldoses. The action of *as*-phenylbenzylhydrazine on dextrose or its phenylbenzylhydrazone leads to the formation of an osazone identical with Neuberg's lævulose-phenylbenzyllosazone.

When dextrophenylbenzylhydrazone is boiled with phenylhydrazine hydrochloride and sodium acetate in dilute alcoholic solution, the product is phenylglucosazone. G. Y.

Decomposition of Nitrocellulose at Temperatures below that of Ignition. A. V. SAPOSCHNIKOFF and M. BORISOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 836—841).—Nitrocellulose decomposes, not only on ignition, but also at temperatures not sufficiently high to ignite it. On heating a mixture of nitrocellulose containing 13.25 per cent. of nitrogen with quartz sand in an electric thermostat at $150^{\circ} \pm 1^{\circ}$, it loses 41.3 per cent. of its weight and decomposes according to the equation: $C_{24}H_{29.31}(NO_3)_{10.7}O_{9.31} = C_{20.14}H_{8.27}O_{22.55}N_4 + 2.58NO + 1.88CO_2 + 1.981CO + 2.06N_2 + 10.52H_2O$. With nitrocellulose containing 12 per cent. of nitrogen, the loss in weight is 43.2 per cent. and the equation expressing the decomposition: $C_{24}H_{30.72}(NO_3)_{9.28}O_{10.72} = C_{20.82}H_{4.8}O_{19.5}N_{2.76} + 1.52NO + 1.42CO_2 + 1.764CO + 2.50N_2 + 12.96H_2O$.

On comparing these results with the following equations, representing the changes on igniting the nitrocellulose: (1) $C_{24}H_{29}(NO_3)_{11}O_9 = 12CO_2 + 12CO + 8.5H_2 + 5.5N_2 + 6H_2O$ and (2) $C_{24}H_{31}(NO_3)_9O_{11} = 6.84CO_2 + 16.51CO + 0.643CH_4 + 7.39H_2 + 4.5N_2 + 4.92H_2O$, it will be seen that the slow combustion occurring at the lower temperatures differs from the ignition in yielding a solid nitrogenous residue, in giving nitric oxide (and, at the beginning of the reaction, nitrogen peroxide), and in yielding no hydrogen but an increased proportion of water. When heated at 150° without sand, the nitrocelluloses decompose more rapidly and completely. Thus, the one containing 13.25 per cent. of nitrogen loses 91.1 per cent. of its weight; 63.2 per cent. of this loss is water and the rest a gaseous mixture having the percentage composition: NO, 27.74; CO_2 , 25.10; CO, 17.44; N_2 , 29.72.

At 135° , gaseous mixtures were obtained from the two nitrocelluloses having the percentage compositions by volume:

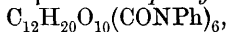
| | Nitrocellulose with 13.25 per cent. N. | Nitrocellulose with 12 per cent. N. |
|--------------|---|--|
| NO..... | 34.52 | 28.33 |
| CO_2 | 29.38 | 21.33 |
| CO | 13.43 | 19.67 |
| N_2 | 22.67 | 30.67 |

T. H. P.

Cellose. LÉON MAQUENNE and W. GOODWIN (*Bull. Soc. chim.*, 1904, [iii], 31, 854—859. Compare Skraup and collaborators, *Abstr.*, 1899, i, 852, and 1901, i, 370).—Cellose, prepared from cellulose by a modification of Skraup's process (*loc. cit.*), furnishes two octoacetyl derivatives. The first form, melting at 228 — 229° and identical with that described by Franchimont and by Skraup, is produced when the sugar is treated with acetic anhydride and sulphuric acid; the second form, obtained when the acetylation is conducted in presence of anhydrous sodium acetate, melts at 196° and is converted instantaneously into the first form by

heating with acetic anhydride and sulphuric acid. With benzoyl chloride, the sugar yields only resinous products.

Cellose furnishes an amorphous *hexaphenylurethane*,



at the same time losing a molecule of water; the *oxime* is amorphous and on hydrolysis furnishes a *glucoarabinose*.

Cellose is oxidised by nitric acid (sp. gr. 1.2) into saccharic acid and by bromine in water into *cellobionic acid*, $\text{C}_{12}\text{H}_{22}\text{O}_{12}$, which, on hydrolysis, yields dextrose and gluconic acid. The salts of cellobionic acid are amorphous and very soluble in water, but less so in alcohol.

T. A. H.

Starch. LEON MAQUENNE (*Ann. Chim. Phys.*, 1904, [viii], 2, 109—134).—A *résumé* of work already published (compare Abstr., 1903, i, 679; this vol., i, 17, 227, 228, 294. Compare also Fernbach and Wolff, this vol., i, 211, 374).

M. A. W.

Compounds of Chromic Chloride with Substituted Ammonias. WILLIAM R. LANG and CHARLES M. CARSON (*J. Amer. Chem. Soc.*, 1904, 26, 758—759. Compare Proc., 1903, 147).—The action of ethylamine on chromic chloride at 0—18° is very vigorous, and dark red crystals of the compound $\text{Cr}_2\text{Cl}_6 \cdot 10\text{EtNH}_2 \cdot 2\text{H}_2\text{O}$ are formed. The latter, when heated at 60°, forms the compound $\text{Cr}_2\text{Cl}_6 \cdot 8\text{EtNH}_2 \cdot 2\text{H}_2\text{O}$. Dimethylamine, diethylamine, trimethylamine, and triethylamine have no effect on chromic chloride. Ethylenediamine reacts violently with chromium chloride at 0—18° with the formation of dark red crystals of the compound $\text{Cr}_2\text{Cl}_6 \cdot 8\text{C}_2\text{H}_4(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$. Aniline, methylaniline, and dimethylaniline have no action on chromic chloride. A. McK.

Density of Asparagine. ARNALDO PIUTTI (*Gazzetta*, 1904, 34, ii, 36—46).—Boggio (*Gazzetta*, 1888, 18, 477) stated that the sp. gr. of *l*-asparagine was 1.548, whilst that of the *d*-isomeride was 1.528 at the same temperature (about 14°/4°). As, however, both Liebisch and Walden found, as the result of the investigation of many optically active compounds, that the specific gravities of optical antipodes are always the same and in general different from that of the racemic compound, the author has made fresh measurements of *d*- and *l*-β-asparagines and of *i*-α-asparagine by the suspension method in a special apparatus; the liquid used was a mixture of bromoform and toluene. It is found that the *d*- and *l*-β-asparagines have the same sp. gr., namely, 1.5434 at 14.8°/4°. The value for *i*-α-asparagine at 14.8°/4° is 1.454.

T. H. P.

Cyanoacetylcyanamide. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 151597).—The potassium and sodium derivatives of ethyl cyanoacetate react very readily with an alcoholic solution of cyanoamide, forming *cyanoacetylcyanamide*, $\text{CN} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CN}$, which crystallises from ether in prisms and melts and decomposes at 93°. It dissolves readily in water, alcohol, or ether, and forms stable, neutral salts with alkalis. Cyanoacetylcyanamide may be employed for the synthesis of pyrimidine derivatives.

C. H. D.

Dimethylpyroarsonic Acid. E. BAUD (*Compt. rend.*, 1904, 139, 411—413).—When anhydrous methylarsonic acid is heated at 120—140° in a current of hydrogen, dimethylpyroarsonic acid is formed: $2\text{H}_2\text{MeAsO}_3 = \text{H}_2\text{Me}_2\text{As}_2\text{O}_5 + \text{H}_2\text{O}$ (−5·207 Cal). The heat of solution of the acid in water is −0·513 Cal. Heated at 170—180° in a current of hydrogen, the acid decomposes into methyl alcohol and arsenious oxide, $\text{H}_2\text{Me}_2\text{As}_2\text{O}_5 = 2\text{MeOH} + \text{As}_2\text{O}_3$. When sodium hydrogen methylarsonate is heated, it loses its water of crystallisation and then yields disodium dimethylpyroarsonate. Disodium methylarsonate heated at 140° in a current of carbon dioxide slowly absorbs the gas with formation of sodium carbonate and disodium dimethylpyroarsonate, $2\text{Na}_2\text{MeAsO}_3 + \text{CO}_2 = \text{Na}_2\text{Me}_2\text{As}_2\text{O}_5 + \text{Na}_2\text{CO}_3$.

H. M. D.

Action of Formaldehyde on Naphtha and its Distillation Products. ALEXANDER M. NASTUKOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 881—898).—The action of formaldehyde on naphtha in presence of concentrated sulphuric acid yields a compound to which the author gives the name *formolite*. This compound is formed mainly from the less volatile fractions, whilst “benzine” (b. p. up to 100°) gives no trace of it. Formolite has the following percentage composition: C, 78·99; H, 7·39; O, 10·95; S, 2·67. It has a yellow or yellowish-brown colour and is amorphous, infusible, and insoluble in the ordinary solvents.

The amount of this compound formed from any sample of crude naphtha or any of its distillation products affords a new means of characterising these substances, the experiment being carried out as follows. Into an ordinary 100 c.c. measuring cylinder are placed a known volume (20—30 c.c.) of the oil and an equal volume of concentrated sulphuric acid, and to the mixture is added half its volume of formaldehyde solution. The whole is then shaken and the tap opened from time to time to admit of the escape of air and other gases; if necessary, the vessel is cooled with water. The mass is diluted with a large quantity of water, and poured into excess of ammonia solution, the solid product being filtered off and washed, firstly with water and afterwards with benzine. It is best to express the main bulk of the contained liquid, for example, by means of a small wine-press; the residual solid is broken up, pressed between filter paper if necessary, and left to dry in the air until of constant weight. The weight of formolite obtained, expressed as a percentage of the weight of oil taken, is the “formolite number.”

As formolite is not obtained from the paraffin hydrocarbons, this reaction may be used to separate the latter from unsaturated cyclic hydrocarbons which do yield it.

The reaction may also be used for testing the purity of hydrocarbons and for preparing new hydrocarbons from the naphthylenes and terpenes (compare Abstr., this vol., i, 242).

T. H. P.

Butylbenzenes. EYVIND BOEDTKER (*Bull. Soc. chim.*, 1904, [iii], 31, 965—971).—*tert.*-Butyl alcohol having n_D 1·38888 at 18·5° and 1·38705 at 25° (compare Brühl, Abstr., 1888, 781) was converted into the corresponding chloride (n_D = 1·38686 at 17·8°), and this was con-

densed with benzene in presence of aluminium chloride; the sole product was *tert.*-butylbenzene, which boiled at 168.2° under 760 mm. pressure and had n_D 1.49724 at 18.5° .

*iso*Butyl alcohol furnished a mixture of *isobutyl* and *tert.*-butyl chlorides (compare Freund, Abstr., 1876, i, 543), and this, when condensed with benzene, yielded principally *tert.*-butylbenzene. In addition, three fractions were obtained boiling at 170 — 172° , 173 — 174° , and 182 — 185° , which are in close agreement with the boiling points assigned to *isobutylbenzene* (Schramm, Abstr., 1889, 127), *sec.*-butylbenzene (Estreicher, Abstr., 1900, i, 213), and *n.*-butylbenzene respectively. Determinations of the refractive indices of the three fractions and the observation that a mixture of the two lower fractions was partially converted into *tert.*-butylbenzene when heated with benzene and aluminium chloride, however, led the author to the conclusion that these three fractions consisted essentially of *isobutylbenzene*. When *isobutyl* alcohol is condensed with benzene by means of sulphuric acid (Verley, Abstr., 1899, i, 424), *tert.*-butylbenzene is the principal product, but there is also formed some *p.*-di-*tert.*-butylbenzene identical with that prepared by Baur (Abstr., 1894, i, 446. Compare Verley, *loc. cit.*) This, on oxidation with chromic acid, yields *p.*-butylbenzoic acid and 2 : 5-di-*tert.*-butylbenzoquinone. The latter crystallises from boiling alcohol in lemon-yellow leaflets, melts at 152.5° , sublimes easily and distils in steam. When treated with hydroxylamine hydrochloride in alcohol, it furnishes a *monoxime*, which separates from alcohol or light petroleum in pale yellow crystals and melts at 209° . On reduction, the quinone furnishes only resinous products, and, similarly, no definite substance could be isolated as the result of its interaction with magnesium methyl iodide. The formation of the quinone is stated to be the first recorded instance in which carbon atoms in a benzenoid nucleus have undergone oxidation in preference to those in lateral groups.

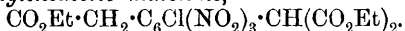
T. A. H.

Derivatives of Trichlorotrinitrobenzene. C. LORING JACKSON and PAUL SHORTT SMITH (*Amer. Chem. J.*, 1904, 32, 168—181).—When 1 : 3 : 5-trichloro-2 : 4 : 6-trinitrobenzene is treated with an alcoholic solution of sodium ethoxide, trinitrophenylroglucinol and its triethyl ether are produced.

Ethyl dichlorotrinitrophenylacetate, $C_6Cl_2(NO_2)_3 \cdot CH_2 \cdot CO_2Et$, obtained by the action of ethyl sodiomalonate on trichlorotrinitrobenzene, crystallises in groups of long, slender, white prisms, melts at 130 — 131° , and is freely soluble in benzene, chloroform, or acetone. When this ester is heated with aniline, *ethyl dianilinotrinitrophenylacetate*, $C_6(NHPh)_2(NO_2)_3 \cdot CH_2 \cdot CO_2Et$, is produced, which crystallises in long, slender, red prisms, melts at 201° , and is soluble in acetone, chloroform, or hot benzene, and insoluble in water; it unites with benzene to produce the additive compound, $C_6(NHPh)_2(NO_2)_3 \cdot CH_2 \cdot CO_2Et, 2C_6H_6$, which forms golden-yellow crystals. If ethyl dichlorotrinitrophenylacetate is heated with concentrated hydrochloric acid at 150 — 160° in a sealed tube, 3 : 5-dichloro-2 : 4 : 6-trinitrotoluene is produced, which crystallises in long, slender, flat, white prisms, melts at 200 — 201° ,

and is soluble in benzene, acetone, chloroform, or hot alcohol, and insoluble in water.

By the action of ethyl sodiomalonate on ethyl dichlorotrinitrophenylacetate, a substance is obtained which crystallises in white needles, melts at 147—148°, is soluble in benzene, chloroform, acetone, ether, carbon disulphide, or hot alcohol, and is probably *ethyl chlorotrinitrophenyleneacetic malonate*,



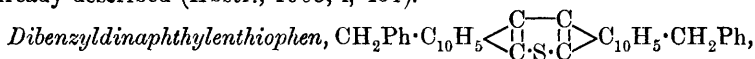
If this compound is heated with strong hydrochloric acid at 160—170° in a sealed tube, 5-chloro-2 : 4 : 6-trinitro-*m*-xylene (m. p. 215—220°) is produced (compare Klages and Knoevenagel, *Abstr.*, 1895, i, 654).

E. G.

Constitution of β -Phenylacenaphthylmethane and its Oxidation Products; β -Benzyl- and β -Benzoyl-naphthalic Acids. CHARLES DZIEWONSKI and MARCUS WECHSLER (*Bull. Soc. chim.*, 1904, [iii], 31, 922—925. Compare this vol., i, 390).—It is now shown that the benzoylnaphthalic acid produced by the oxidation of the phenylacenaphthylmethane already described (*loc. cit.*) is a β -derivative. From this observation, it follows that in the parent hydrocarbon the benzyl group must occupy position 1 or 2 in the acenaphthene nucleus. The readiness with which phenylacenaphthylmethane is dehydrogenated by sulphur, forming tribenzyldecacyclene as one product (see succeeding abstract), leads the authors to regard position 2 as the more probable location of the benzyl group. On this supposition, the oxidation products are the 3-benzoylnaphthalic and 3-benzoylnaphthalic acids.

T. A. H.

Synthesis of a New Yellow Hydrocarbon, Tribenzyldecacyclene (Tribenzyltrinaphthylbenzene), and of a Red Thiophen Derivative, Dibenzyldinaphthylthiophen. CHARLES DZIEWONSKI (*Bull. Soc. chim.*, 1904, [iii], 31, 925—932. Compare this vol., i, 84, 390, and preceding abstract).—[With ELIGIO DOTTA.]—The following substances are simultaneously produced when a mixture of 2-phenylacenaphthylmethane with sulphur is heated as already described (*Abstr.*, 1903, i, 431).



crystallises from benzene in small, bright red needles, melts at 207—210°, is soluble in chloroform and in boiling benzene and its homologues, and slightly so in ether and alcohol; the solution in cold sulphuric acid is violet. It does not form an additive product with picric acid. Chromic acid oxidises it to 3-benzoylnaphthalic acid, indicating that in the parent substance a benzyl group occupies either the 3- or 6-position in each of the naphthalene nuclei.

Tribenzyldecacyclene, $\text{C}_6[\text{C}_{10}\text{H}_5 \cdot \text{CH}_2\text{Ph}]_3$, crystallises from benzene or aniline in small, yellow needles, melts at 270°, and is almost insoluble in alcohol, ether, or boiling acetic acid; dilute solutions show a strong green fluorescence; the solution in sulphuric acid is green. The hydrocarbon does not form an additive product with picric acid. On

oxidation with chromic acid in presence of acetic acid, a brown, amorphous substance is formed. T. A. H.

Benzoylacenaphthene. GUSTAVE PERRIER (*Bull. Soc. chim.*, 1904, [iii], 31, 859—862. Compare Abstr., 1900, i, 331).—The author points out that this compound and its derivatives, recently obtained by Graebe and Haas (Abstr., 1903, i, 409), had already been described by Louïse and himself (Abstr., 1892, 1205, and *Thèse inaug.*, Paris, 1896). T. A. H.

Triphenylmethane Dyes from Dimethyl- and Diethyl-*p*-toluidines. LEOPOLD CASSELLA & Co. (D.R.-P. 149322).—Tetra-alkyldiaminobenzhydrols condense with dialkyl-*p*-toluidines in presence of concentrated sulphuric acid, and by oxidising the resulting leucobases, brilliant bluish-green dyes are obtained. *p*-Toluidine and its monoalkyl derivatives yield only dull shades. The methane carbon atom in the new derivatives probably occupies the *meta*-position to the dialkylamino-group. C. H. D.

Detection of Aldehydic Compounds; Constitution of Nitrosodimethylaniline. GIUSEPPE VELARDI (*Gazzetta*, 1904, 34, ii, 66—74).—The author finds that the reaction described by Angeli and Angelico (this vol., i, 172; ii, 115) and by Rimini (Abstr., 1901, i, 450), in which a compound capable of giving up the NOH-group acts on an aldehyde, is applicable generally and may be used for the detection of unsaturated aldehydes in complex mixtures such as natural oils. The hydroxamic acid formed is not, however, the only product, as the free NOH-group acts simultaneously on the double linking of the unsaturated aldehyde, forming the corresponding oxime; the yield of the latter increases with the number of double linkings in the molecule. Mixed aldehydes behave, in this reaction, similarly to the unsaturated ones, and the same is the case with nitroso-compounds, the constitution of which may be determined in this way.

The method adopted by the author for detecting the presence of an aldehyde in a natural oil is to mix a few drops of the oil with a trace of benzenesulphohydroxamic acid and alcoholic potassium hydroxide and heat the mixture; after cooling, the mass is diluted with water and a little ether added, the aqueous liquid being then neutralised with hydrochloric acid and tested with ferric chloride. Of a number of vegetable oils examined in this way by the author, the majority developed red colorations and a few gave yellow ones. Some of the salts of the hydroxamic acids are described.

Copper cinnamylhydroxamate, $\text{CHPh}:\text{CH}\cdot\text{C}\begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{NO} \end{smallmatrix}\text{Cu}$, is precipitated from solution in 25 per cent. sulphuric acid by means of sodium acetate in minute, emerald-green crystals.

Citronellalhydroxamic acid,



is deposited from light petroleum in white crystals melting at 72—74°. The copper salt, $\text{C}_{10}\text{H}_{17}\text{O}_2\text{NCu}\cdot 2\text{H}_2\text{O}$, forms a green, crystalline powder.

Geranylhydroxamic acid, $\text{CMe}_2:\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}:\text{CH}\cdot\text{C}(\text{OH})\cdot\text{NOH}$, is a heavy oil; its copper salt, $\text{C}_{10}\text{H}_{15}\text{O}_2\text{NCu}$, was analysed.

Copper glycolhydroxamate, $\text{OH}\cdot\text{CH}_2\cdot\text{C}\begin{smallmatrix} \text{O} \\ \diagup \diagdown \end{smallmatrix}\text{NO}\text{Cu}$, is precipitated from solution in dilute sulphuric acid by means of sodium acetate in minute, dark green crystals.

The *barium* salt of *dimethylaminonitrosophenylhydroxylamine*,
 $[\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{NO})\cdot\text{O}]_2\text{Ba}$,
 separates from aqueous solution in minute, faintly yellow crystals.

T. H. P.

Protocatechuic Anilide. PAUL THIBAUT (*Bull. Soc. chim.*, 1904, [iii], 31, 920—922).—Protocatechuic acid (30 grams) is heated with aniline (60 grams) at 100° until solution is complete; phosphorus oxychloride (15 grams) is then added gradually and the mixture is heated at 150° until hydrogen chloride is no longer evolved. The anilide is extracted with an aqueous solution of sodium carbonate. It forms prismatic crystals, melts at $154\text{--}156^\circ$, and is soluble in alcohol, ether, and chloroform. At 180° , it is resolved into its generators.

The method suggested by Schiff (*Abstr.*, 1883, 335) for the preparation of protocatechuic anilide yields an impure product containing arsenic.

T. A. H.

Action of Acid Chlorides on Tertiary Bases containing an Aromatic Radicle. VICTOR AUGER (*Compt. rend.*, 1904, 139, 299—301. Compare Hess, *Abstr.*, 1885, 783).—At temperatures between 200° and 250° , the aliphatic acid chlorides react quantitatively with tertiary bases of the type $\text{NR}^1\text{R}^{11}\text{R}^{111}$ to form the substituted acid amide and alkyl chloride according to the equation $\text{NR}^1\text{R}^{11}\text{R}^{111} + \text{RCOCl} = \text{RCONR}^1\text{R}^{11} + \text{R}^{111}\text{Cl}$, where R^1 and R represent aromatic and aliphatic radicles respectively, R^{11} having a lower molecular weight than R^{111} . *Acetylbenzylanilide*, $\text{COMe}\cdot\text{NPh}\cdot\text{CH}_2\text{Ph}$, obtained by the gradual addition of acetyl chloride to dibenzylaniline at 200° , forms colourless, tabular crystals melting at 58° , slightly soluble in boiling water or cold light petroleum, and very readily soluble in other neutral solvents. *Acetylethylanilide* is similarly prepared from benzylethylaniline. *Methylvaleranilide*, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NPhMe}$, obtained by heating a mixture of isovaleryl chloride and dimethylaniline at 220° , boils at 170° under 50 mm. pressure and forms large crystals melting at 22° , is insoluble in water and very soluble in other neutral solvents, and is identical with the compound obtained by the action of isovaleryl chloride on a molecular mixture of pyridine and methylaniline. Attempts to replace the second aliphatic radicle of the base by a second acyl radicle were unsuccessful.

M. A. W.

Alkyl Esters of 3:4-Diaminobenzoic Acid. EDUARD RITSERT and WILHELM EPSTEIN (*D.R.-P.* 151725).—The aminocarboxylic esters are employed with difficulty as local anæsthetics on account of their insolubility, and their soluble salts react so strongly acid as to be unsuitable (compare this vol., i, 413, 414). The solubility and basicity of the esters is greatly increased by the introduction of a second amino-group.

Ethyl p-acetylaminobenzoate, prepared by acetylating ethyl *p*-amino-

benzoate, melts at 110° , and on nitration yields ethyl 3-nitro-4-acetylaminobenzoate, melting at $96-97^{\circ}$ (compare Thieme, Abstr., 1891, 915). Alcoholic hydrogen chloride hydrolyses this to ethyl *m*-nitro-*p*-aminobenzoate, melting at 136° (compare Grohmann, Abstr., 1890, 305, and Thieme, *loc. cit.*). Alcoholic stannous chloride reduces this to ethyl 3:4-diaminobenzoate, crystallising from hot water in bundles of white needles and melting at $112-113^{\circ}$. It dissolves in $1/4$ of the theoretical quantity of hydrochloric acid, the solution having only a faintly acid reaction. *p*-Aminobenzoic acid may be acetylated by heating its sodium salt with glacial acetic acid, and then nitrated. After hydrolysis and reduction, the product is readily esterified by warming with hydrogen chloride and methyl alcohol, yielding methyl 3:4-diaminobenzoate, crystallising in white needles, melting at $108-109^{\circ}$, and dissolving more readily in cold water than the ethyl ester.

C. H. D.

Acetyl-*p*-aminophenylglycine. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 152012).—Acetylphenylglycine does not yield a nitro-derivative with nitric acid alone (Paal and Otten, Abstr., 1890, 1415), but is readily nitrated in sulphuric acid solution at $0-5^{\circ}$. Acetyl-*p*-nitrophenylglycine crystallises from glacial acetic acid in light brown leaflets, melts at $191-192^{\circ}$, and dissolves in alkalis to a pale yellow solution. Iron and dilute acetic acid reduce it on warming to acetyl-*p*-aminophenylglycine, which is very readily soluble in water and cannot be isolated in the solid state. Its diazonium compound is pale yellow, and forms a crimson dye with 1:8-dihydroxynaphthalene-3:6-disulphonic acid.

C. H. D.

Preparation of Acetylphenylglycine-*o*-carboxylic Acid. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 151435. Compare Abstr., 1901, i, 709).—The salts of phenylglycine-*o*-carboxylic acid are partly converted into indoxyl derivatives by heating with acetic anhydride. The acetyl derivative is, however, obtained quantitatively on adding acetic anhydride in cold aqueous suspension to the acid salts.

C. H. D.

Orthophosphoric Anilide and its Homologues; Non-existence of the Compound $\text{NPh}\cdot\text{P}(\text{NPh})_2$. PAUL LEMOULT (*Compt. rend.*, 1904, 139, 206—208).—The chlorotetra-anilides, $\text{PCl}(\text{NHR})_4$, which are formed by the prolonged action of phosphorus pentachloride on the amines (compare Abstr., 1897, i, 463), readily lose hydrochloric acid on boiling with alcoholic potash, anilides of phosphoric acid and primary amines resulting according to the equations: (1) $\text{PCl}(\text{NHR})_4 = \text{P}(\text{NHR})_3\cdot\text{NR} + \text{HCl}$; (2) $\text{P}(\text{NHR})_3\cdot\text{NR} + \text{H}_2\text{O} = \text{PO}(\text{NHR})_3 + \text{NH}_2\text{R}$. When sodium ethoxide in absolute alcohol is used instead of alcoholic potash, the second reaction cannot take place, and the product obtained is the intermediate compound, $\text{P}(\text{NHR})_3\cdot\text{NR}$.

The substance obtained by Gilpin (Abstr., 1902, i, 700) by the action of phosphorus pentachloride on aniline dissolved in benzene and treatment of the product with boiling water, to which he assigned

the formula $P(NPh)_2 \cdot NPh$, is, in reality, orthophosphoric anilide, $PO(NHPh)_3$, melting at 212° .

The homologue obtained from *m*-xylidine crystallises in large, silky needles melting at 225° .

On heating the anilide and its homologues somewhat above their respective melting points, they lose a molecule of the amine and probably yield substances of the type $PO(NR) \cdot NHR$. H. M. D.

Some Derivatives of Pentabasic Phosphoric Acid, $P(OH)_5$. P. LEMOULT (*Compt. rend.*, 1904, 139, 409—411. Compare this vol., i, 380).—The reaction between the chlorotetra-anilides of the type $PCl(NHR)_4$ and the sodium alkyloxides depends on the nature of the radicle R. If R is the phenyl group, trianilinophenylphosphimide, $P(NPh)(NHPh)_3$, is obtained whichever alkyloxide is employed. If R is a homologue of phenyl, the products obtained vary with the nature of the alkyloxide, but can be represented by the general formula $P(OR^1)(NHR)_4$, where R^1 is the radicle of the alkyloxide.

To obtain these substances, phosphorus chlorotetra-anilide is suspended in boiling alcohol, and the calculated quantity of the corresponding sodium alkyloxide is added; the hot solution is then filtered and allowed to crystallise. The analysis of the products, and the action of hydrochloric acid on them, indicate that alcohol of crystallisation is present.

The compound $P(NH \cdot C_6H_4Me)_4 \cdot OEt, EtOH$ forms large, white crystals melting at 114° , at which temperature decomposition takes place.

The compound $P(NH \cdot C_6H_3Me_2)_4 \cdot OMe, MeOH$ is obtained in the form of lustrous spangles or in crystals melting at 98° and resembling the preceding compound.

The compound $P(NH \cdot C_6H_3Me_2)_4 \cdot OEt, EtOH$ forms fine needles melting at 107° . These substances are soluble in hot alcohol, are decomposed by boiling acetic acid and benzene, and are saponified by alkalis. By the action of hydrochloric acid in alcoholic solution, the original chlorotetra-anilide is obtained. H. M. D.

Decomposition of Nitroso-compounds. WILLIAM A. NOYES and RENE DE M. TAYEAU (*Amer. Chem. J.*, 1904, 32, 285—293).—The nitroso-compound prepared from aminolauroic anhydride, and melting at 138 — 139° (Bredt, Abstr., 1902, i, 374), is decomposed by cold sodium hydroxide and alcohol, forming a hydrocarbon, C_8H_{14} , isolauroic acid, $C_8H_{14} \cdot CO_2H$, a hydroxy-acid, a lactone, and a condensation product.

The hydroxy-acid, $OH \cdot C_8H_{14} \cdot CO_2H$, boils at 180 — 185° under 25 mm. pressure and is identical with that prepared from ethyl aminolauroate and nitrous acid. The lactone is isocampholactone, $C_8H_{14} \begin{smallmatrix} \diagup CO \\ \diagdown O \end{smallmatrix}$, melting at 32° (compare Abstr., 1895, i, 295, and Bredt, *loc. cit.*). A 5 per cent. alcoholic solution has $[\alpha]_D - 60.7^\circ$. The silver salt of the corresponding acid, $OH \cdot C_8H_{14} \cdot CO_2Ag$, was prepared.

The condensation product, $(C_8H_{14} \begin{smallmatrix} \diagup CO \\ \diagdown N \cdot C_2H_4O \end{smallmatrix})_2$, crystallises from

light petroleum in large, faintly yellow plates and melts at 140° . It is almost insoluble in water, but dissolves in dilute hydrochloric acid and is reprecipitated by ammonia. When methyl alcohol is used in the preparation instead of ethyl alcohol, a compound, $(C_{10}H_{16}O_2N)_2$, crystallising from light petroleum in leaflets and melting at 99° is obtained. The molecular weight was determined cryoscopically in benzene solution. The reaction has some analogy with the formation of acetaldehyde from diazonium compounds and ethyl alcohol.

On filtering off the condensation product obtained from sodium hydroxide, methyl alcohol, and the nitroso-compound and acidifying, a white, dibasic acid, probably $CO_2H \cdot C_8H_{14} \cdot N \cdot N \cdot C_8H_{14} \cdot CO_2H$, melting at $327-328^{\circ}$ (corr.), is obtained. C. H. D.

Preparation of Nerol from Petit Grain Oil. HEINE & Co. (D.R.-P. 150495).—The terpene alcohol, nerol, $C_{10}H_{18}O$, obtained by Hesse and Zeitschel from neroli oil (Abstr., 1903, i, 189) may also be prepared from petit grain oil. The oil is saponified and distilled with steam or under reduced pressure, and after removal of terpenes and linalool the following fraction is converted into the phthalic ester and purified. After hydrolysis, a mixture of 40 per cent. nerol and 60 per cent. geraniol is obtained. The geraniol is separated by means of dry calcium chloride, and the nerol thus obtained is rectified. Nerol is optically inactive and forms an additive compound with four atoms of bromine. Its physical properties are identical with those of the nerol prepared from neroli oil. C. H. D.

Preparation of Vanillin. F. FROGER-DELAPIERRE (D.R.-P. 150981).—In the oxidation of eugenol or isoeugenol by ozone, resin is generally produced. This is avoided and a good yield of vanillin obtained by using air previously rendered active by passing through a terpene, sesquiterpene, or similar hydrocarbon. Thus the air may be caused to bubble through a layer of turpentine at $30-35^{\circ}$, then to pass through a plate-column at $80-90^{\circ}$, and finally over a layer of isoeugenol heated at 100° , and rendered neutral or slightly alkaline. When phenols containing an allyl group are to be oxidised, a mixture of 1 vol. of oxygen with 2 vols. of carbon dioxide is to be employed in preference to air. C. H. D.

Isomeric Ethers of Pyrogallol. II. JOSEF HERZIG and JACQUES POLLAK (*Monatsh.*, 1904, 25, 501-519. Compare Abstr., 1903, i, 89, 346; Graebe and Martz, Abstr., 1903, i, 262).—2 : 3-Dihydroxy-4-methoxybenzene-1-carboxylic acid, obtained by hydrolysis of its methyl ester, crystallises in long, white needles and melts at $204-206^{\circ}$. When heated at 230° , the acid loses carbon dioxide and yields 1-methoxy-2 : 3-dihydroxybenzene, which crystallises in needles, melts at $37-40^{\circ}$, and boils at $146-147^{\circ}$ under 15-16 mm. pressure. The diacetyl derivative, $C_6H_3(OMe)(OAc)_2$, crystallises in white leaflets and melts at $91-93^{\circ}$.

On oxidation, 2 : 3-dimethoxyphenol, unlike its 2 : 6-isomeride, gives no cærulignone reaction. The benzoyl derivative of 2 : 3-dimethoxy-

phenol crystallises in long, colourless needles and melts at 55—57°; the benzoyl derivative of 2:6-dimethoxyphenol melts at 118°.

In the formation of 2-hydroxy-3:4-dimethoxybenzene-1-carboxylic acid, a small amount of 2:3:4-trimethoxybenzene-1-carboxylic acid is formed. 1:2:3-Trimethoxybenzene is formed by the action of methyl iodide and potassium hydroxide on 2:3-dimethoxyphenol in aqueous methyl-alcoholic solution. G. Y.

4-Formylamino- α -naphthol. FRANZ GAESS (D.R.-P. 149022).—4-Amino- α -naphthol is readily formylated by heating the hydrochloride with sodium formate and concentrated formic acid. The hydroxyl group is not attacked. 4-Formylamino- α -naphthol crystallises from water in rosettes of small, colourless needles, melts at 168°, and dissolves readily in alcohol. The acetyl group cannot be introduced in the same manner, the use of acetic anhydride being necessary.

C. H. D.

Disazo-dyes from 6-Amino- α -naphthol-3-sulphonic Acid. K. OEHLER (D.R.-P. 151332).—The azo-compounds prepared by combining diazonium salts with 6-amino- α -naphthol-3-sulphonic acid react in alkaline solution with diazotised nitro-derivatives of *o*-aminophenol to form disazo-dyes. *o*-Diazophenol does not combine, but any of its derivatives containing at least one nitro-group may be employed. The preparation of dyes from picramic acid and from 3-nitro-5-amino-4-hydroxybenzoic acid is described.

C. H. D.

Acyl Derivatives of Alkyl Ethers of Rufigallol. CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING (D.R.-P. 151724).—The acyl derivatives of rufigallol possess purgative properties. *Diacetylrufigallol tetramethyl ether*, $C_{22}H_{20}O_{10}$, crystallises from acetic acid or alcohol in yellow masses and melts at about 180—190°. It is insoluble in water, but dissolves sparingly in alcohol. *Diacetylrufigallol tetraethyl ether*, $C_{26}H_{28}O_{10}$, separates from chloroform and alcohol in yellow crystals and melts at 230—235°. *Benzoylrufigallol tetramethyl ether*, prepared by alkaline benzoylation, is precipitated from chloroform solution by alcohol as a brown powder and melts at 190—205°.

C. H. D.

Synthesis of Alcohols of the cycloHexane Series. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1904, 139, 343—346).—Magnesium cyclohexyl chloride, obtained by the action of magnesium on cyclohexyl chloride in presence of iodine readily reacts with aldehydes and ketones, giving a crystalline mass which is decomposed by water with the production of alcohols of the cyclohexane series. The alcohols thus produced lose water on heating with anhydrous zinc chloride, and unsaturated hydrocarbons are obtained.

*cyclo*Hexylcarbinol, $C_6H_{11}\cdot CH_2\cdot OH$ (compare Abstr., 1903, i, 673), is obtained from trioxymethylene; it has an odour resembling that of camphor, boils at 181° under 755 mm. pressure, has a sp. gr. 0.944 at 0°/0°. The hydrocarbon, $C_6H_{10}\cdot CH_2$, which it yields, boils at 105°, and has a sp. gr. 0.828 at 0°/0°. By action of ethyl orthoformate on magnesium cyclohexyl chloride in ethereal solution, a solid mass is obtained

which with water gives the acetal, $C_6H_{11} \cdot CH(OC_2H_5)_2$, an oily liquid boiling at $109-110^\circ$ under 20 mm. pressure. When boiled with dilute sulphuric acid, it yields the aldehyde, $C_6H_{11} \cdot COH$, a liquid boiling at 155.5° under 755 mm. pressure.

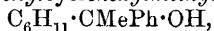
cycloHexylmethylcarbinol, $C_6H_{11} \cdot CHMe \cdot OH$, previously obtained by Bouveault (compare this vol., i, 61), is a liquid boiling at 189° under 755 mm. pressure, and having a sp. gr. 0.9456 at $0^\circ/0^\circ$. The hydrocarbon, $C_6H_{10} \cdot CH \cdot CH_3$, boils at 135° , sp. gr. 0.842 at 0° .

cycloHexylisobutylcarbinol, $C_6H_{11} \cdot CH(OH) \cdot CHMeEt$, is obtained from isovaleraldehyde; it is a liquid boiling at 123° under 20 mm. pressure, sp. gr. 0.916 at $0^\circ/0^\circ$. On oxidation with chromic acid, it yields the ketone, $C_6H_{11} \cdot CO \cdot CHMe_2$, boiling at 114° under 20 mm. pressure. The corresponding oxime melts at 77° .

cycloHexyldimethylcarbinol, $C_6H_{11} \cdot CMe_2 \cdot OH$, the product obtained from acetone, is a liquid of strong camphoraceous odour which boils at 96° under 20 mm. pressure and has a sp. gr. 0.938 at $0^\circ/0^\circ$. The corresponding hydrocarbon, $C_6H_{10} \cdot C(Me)_2$, boils at 151° under 760 mm. pressure and has a sp. gr. 0.864 at $0^\circ/0^\circ$.

Benzaldehyde yields *phenylcyclohexylcarbinol*, $C_6H_{11} \cdot CHPh \cdot OH$, a crystalline solid melting at 41° and boiling at 168° under 20 mm. pressure, very soluble in alcohol and ether. The hydrocarbon, $C_6H_{10} \cdot CHPh$, boils at 138° under 20 mm. pressure and has a sp. gr. 0.982 at $0^\circ/0^\circ$. On oxidising the alcohol, the ketone, $C_6H_{11} \cdot C(=O)Ph$, melting at 51° , is obtained.

Acetophenone yields *phenylcyclohexylmethylcarbinol*,



a liquid boiling at 168° under 20 mm. pressure and having a sp. gr. 1.043 at $0^\circ/0^\circ$; it yields the hydrocarbon, $C_6H_{10} \cdot CMePh$, boiling at 159° under 36 mm., or at 260° under 755 mm. pressure, and has a sp. gr. 0.981 at $0^\circ/0^\circ$.

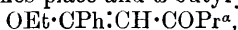
Benzophenone behaves differently, the products resulting from the reaction being *cyclohexene* and *benzhydrol*.

From ethyl formate, *dicyclohexylcarbinol*, $CH(C_6H_{11})_2 \cdot OH$, which melts at 63° and boils at 166° under 20 mm. pressure, is obtained. Chromic acid converts it into the ketone, $C_6H_{11} \cdot CO \cdot C_6H_{11}$, a liquid boiling at 159° under 20 mm. pressure, and having a sp. gr. 0.986 at $0^\circ/0^\circ$. With magnesium *cyclohexyl chloride*, the ketone does not give *tricyclohexylcarbinol*, but *dicyclohexylcarbinol* and *cyclohexene* are obtained. The hydrocarbon, $C_6H_{10} \cdot CH \cdot C_6H_{11}$, boils at 133° under 20 mm. pressure and has a sp. gr. 0.919 at $0^\circ/0^\circ$. H. M. D.

Amino-derivatives of Hydroxybenzyl Alcohols. FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 148977).—Amino-hydroxybenzyl alcohols and their ethers and esters may be prepared by the reduction of nitrohydroxybenzyl alcohols and their ethers, or of the esters prepared by the action of acids on nitrohydroxybenzyl chlorides (Abstr., 1903, i, 338). 3-Amino-6-hydroxybenzyl alcohol, $OH \cdot C_6H_3(CH_2 \cdot OH) \cdot NH_2$, prepared by reducing the nitro-compound with tin and hydrochloric acid, crystallises from alcohol in colourless leaflets, becoming brown in air, and melts and darkens at $135-142^\circ$. The salts are stable. The *methyl ether* forms colourless leaflets, melts

at 124—126°, and dissolves sparingly in water. The *ethyl ether* is similar, and melts at 76—78°. 3-Nitro-6-hydroxybenzyl acetate, from the corresponding chloride with acetic acid and sodium acetate, crystallises from water in yellow needles and melts at 105—107°. 3-Amino-6-hydroxybenzyl acetate forms crusts of needles and leaflets and melts at 136—137°. 3-Amino-2-hydroxybenzyl alcohol forms colourless needles and melts at 112—114°. All these bases become brown in air, but form stable salts.
C. H. D.

Condensation of Acetylenic Ketones with the Alcohols and Phenols. CHARLES MOUREU and M. BRACHIN (*Compt. rend.*, 1904, 139, 208—210. Compare this vol., i, 286).—When phenylbutyrylacetylene, $\text{CPh:C}\cdot\text{COPr}^a$, is treated with sodium ethoxide in ethyl alcohol, condensation takes place and ω -butyryl- α -ethoxystyrene,



is formed; this melts at 137—138°, boils at 155—158° under 10 mm. pressure, and has a sp. gr. 1.013 at 20°/0°. The reaction takes place more readily, and a better yield is obtained if a little phenol is added to the alcohol. On warming with dilute sulphuric acid, the product is completely hydrolysed, and butyrlacetophenone, $\text{CPh}\cdot\text{CH}_2\cdot\text{COPr}^a$, is formed.

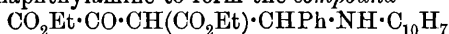
In a similar way, ω -propionyl- α -ethoxystyrene, $\text{OEt}\cdot\text{CPh:CH}\cdot\text{COEt}$, results from the condensation of propionylphenylacetylene with ethyl alcohol. It is a colourless oil, distils at 167—170° under 18 mm. pressure, and has a sp. gr. 0.972 at 20°/0°; on hydrolysis, it yields propionylacetophenone.

The phenols are found to react in the same manner. ω -Butyryl- α -phenoxytyrene, $\text{OPh}\cdot\text{CPh:CH}\cdot\text{COPr}^a$, crystallises from light petroleum in beautiful prisms, melts at 55°, boils at 206—209° under 11 mm. pressure, and yields butyrlacetophenone on hydrolysis. ω -Propionyl- α -guaiacyloxytyrene, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CPh:CH}\cdot\text{COEt}$, is obtained by condensation of propionylphenylacetylene with guaiacol. It crystallises readily from light petroleum, melts at 76—77°, boils at 231° under 17 mm. pressure, and yields propionylacetophenone on hydrolysis (compare *Abstr.*, 1903, i, 581).
H. M. D.

Preparation of Organic Acids from Petroleum NICOLAI ZELINSKY (*D.R.-P.* 151880).—The reaction between magnesium and chlorinated paraffins is very incomplete, but may be rendered complete by the addition of a catalytic agent, such as iodine, aluminium haloids, or hydrogen chloride. The fractions obtained in the distillation of petroleum may be converted into the corresponding carboxylic acids by chlorinating, adding magnesium and a catalytic agent, passing a current of carbon dioxide, and decomposing the complex magnesium compound thus obtained. The yield may amount to 60 per cent. of the theoretical. Pentane yields isohexic acid; a naphthene fraction boiling at 80—82° yields pure cyclohexanecarboxylic acid, and a naphthene fraction boiling at 71—79° yields heptic, methylcyclopentanecarboxylic, and cyclohexanecarboxylic acids.
C. H. D.

Action of Ethyl Oxalacetate on Benzaldehyde in Presence of Primary Amines. LOUIS J. SIMON and A. CONDUCHÉ (*Compt. rend.*, 1904, 139, 211—212).—Ethyl oxalacetate condenses with the aldehydes in the presence of ammonia, and substituted derivatives of diketodihydropyrrolinecarboxylic acid are obtained (compare this vol., i, 521). The same reaction takes place when the ammonia is replaced by primary fatty and aromatic amines. The substitution product obtained from aniline by warming a mixture of ethyl oxalacetate, benzaldehyde, and aniline in molecular proportions on the water-bath, or by acting in the cold on the oxalacetate with an alcoholic or ethereal solution of benzylideneaniline, melts at 173° and gives a phenylhydrazone melting at 150°. The product obtained from *p*-toluidine melts at 159°; *o*-toluidine apparently does not undergo this condensation. H. M. D.

Action of Ethyl Oxalacetate on Aromatic Aldehydes in the Presence of β -Naphthylamine. LOUIS J. SIMON and A. CONDUCHÉ (*Compt. rend.*, 1904, 139, 297—299. Compare this vol., i, 521).—Ethyl oxalacetate reacts with benzaldehyde and β -naphthylamine or with benzylidene- β -naphthylamine to form the compound



and not a derivative of diketodihydropyrrolinecarboxylic acid, as stated by Schiff and Bertini (compare Abstr., 1897, i, 293). The new compound crystallises in white needles melting at 162°, loses H_2O on treatment with concentrated sulphuric acid to form a yellow or orange crystalline compound, $\text{C}_{25}\text{H}_{23}\text{O}_4\text{N}$, melting at 146—147°, which on oxidation with chromic acid is converted quantitatively into the compound $\text{C}_{25}\text{H}_{21}\text{O}_4\text{N}$, crystallising in white needles, melting at 128°, containing two carboxy-groups, and yielding on hydrolysis an acid, probably phenylnaphthaquinolinedicarboxylic acid, melting at 215—220°, and slightly soluble in boiling water or alcohol. By the action of alcoholic potassium hydroxide on the yellow compound melting at 146—147°, a basic compound, probably phenylnaphthaquinoline, melting at 189°, is obtained. Analogous compounds are obtained when the benzaldehyde is replaced by anisaldehyde or *m*-nitrobenzaldehyde, whilst piperonal yields a derivative of diketodihydropyrrolinecarboxylic acid; salicylaldehyde or vanillin gives a negative result. M. A. W.

Reduction of *o*-Quinones. FRANZ KNESCH (D.R.-P. 151981).—The reduction of *o*-quinones derived from polynuclear hydrocarbons to the corresponding *o*-dihydroxy-compounds by sulphur dioxide is incomplete, and when the reaction occurs under pressure partial decomposition often takes place. Almost pure products may be obtained by reducing the sodium hydrogen sulphite compounds of *o*-quinones by iron or zinc dust without the addition of acids or alkalis. Salts of hyposulphurous acid are formed, which act as reducing agents.

9:10-Dihydroxyphenanthrene, from phenanthraquinone, forms a *dibenzoyl* derivative melting at 230—231°. *Dihydroxychrysene*, from chrysoquinone, is white and melts at 152—154°, the *diacetyl* derivative melts at 225—228°, and the *dibenzoyl* derivative at 241—242°.

Dihydroxyretene forms a *diacetyl* compound melting at 170—171° and a *dibenzoyl* compound melting at 231—232°. C. H. D.

Electrolytic Oxidation of Organic Compounds. FARBERWERKE VORM. MEISTER, LUCIUS, & BRUNING (D.R.-P. 152063).—Many organic compounds may be electrolytically oxidised in a bath containing cerium salts. The ceric compound produced at the anode is at once reduced to cerous salt by the organic compound, so that in a well-conducted operation the solution remains colourless throughout. No diaphragm is necessary, and the compound to be reduced may be either in solution or in fine suspension.

Anthracene is best suspended in 20 per cent. sulphuric acid containing 2 per cent. of cerous sulphate and electrolysed with a current of 5 amperes per sq. dm. and a potential difference of 2·8—3·5 volts, the temperature being 80—90°, raised at the end to 100°. Naphthalene yields naphthaquinone and, on further oxidation, phthalic acid. Phenanthrene requires a more concentrated cerium solution, and yields phenanthraquinone, or, on further oxidation, diphenic and benzoic acids. C. H. D.

Chloro-derivatives of β -Hydroxyanthraquinones. R. WEDEKIND & Co. (D.R.-P. 152175).—Alkaline solutions of hypochlorites oxidise alizarin and other hydroxyanthraquinone dyes, and also the non-dyeing α -hydroxyanthraquinones, such as anthrarufin, almost instantaneously. On the other hand, the non-dyeing β -hydroxyanthraquinones are converted by this treatment into chloro-derivatives: $\text{RH} + \text{NaOCl} = \text{RCl} + \text{NaOH}$. Monochloro-derivatives are generally obtained in strongly alkaline solution; in presence of alkali carbonates, higher substituted derivatives may be obtained. A temperature of 30—40° is desirable, some alkali hydrogen carbonate being added to fix the alkali hydroxide formed. Anthraflavic acid yields, according to the conditions of experiment, a mono-, di-, or trichloro-derivative. The preparation of *dichloroisanthraflavic acid* and of *chloro- β -hydroxyanthraquinone* is also described. On fusion, chlorine and hydrogen chloride are evolved, but the chlorine is nevertheless firmly combined, not being removed, in the case of trichloroanthraflavic acid, by heating for 14 hours at 220° with milk of lime.

C. H. D.

[Bromo-derivatives of Arylaminoanthraquinones.] FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 151512 and 151513).—2:4-Dibromo-5-nitro-1-aminoanthraquinone, prepared by brominating 5-nitro-1-aminoanthraquinone in water, crystallises from pyridine or nitrobenzene in short, thick, red needles and is insoluble in water, alkalis, or dilute acids. It condenses with *p*-toluidine in presence of sodium acetate, yielding 2-bromo-1-amino-4:5-di-*p*-toluidinoanthraquinone, which crystallises from pyridine in bronze needles. Other arylamino-groups may be introduced in the same manner. Soluble blue dyes are obtained on sulphonating these compounds with fuming sulphuric acid.

C. H. D.

Introduction of Amine Residues into Hydroxyanthraquinones. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 151511).—Three aniline residues may be introduced into purpurin, hydroxyanthrapurpurin, or hydroxyflavopurpurin by heating with aniline and boric acid for 2 hours at 140—150°, and finally at 180—185° until the bluish-green colour becomes permanent.

Trianilinoanthraquinone crystallises from aniline or pyridine in black needles and dissolves in chloroform to a bluish-green solution. The product from hydroxyflavopurpurin and aniline forms metallic needles. The solutions in concentrated sulphuric acid are yellow, becoming red on warming. C. H. D.

Compound of Santalol and Formaldehyde. ALFRED STEPHAN (D.R.-P. 148944).—Santalol combines with formaldehyde in presence of dilute mineral acids at 95—100°. The compound, $C_{16}H_{18}O_2$, formed is a yellow, balsam-like oil and has a sp. gr. 0.882 and $[\alpha]_D^{20}$ 10.9° at 20° in chloroform solution. Warm water on distillation decomposes it into santalol and formaldehyde. C. H. D.

Galloflavin and Resoflavin. JOSEF HERZIG and RUDOLF TSCHERNE (*Monatsh.*, 1904, 25, 603—610. Compare Bohn and Graebe, Abstr., 1887, 1167).—Analytical results obtained with galloflavin and its acetyl derivative agree with the formulæ $C_{15}H_8O_{10}$ and $C_{15}H_3O_5(OAc)_5$ better than with Bohn and Graebe's formulæ, $C_{13}H_6O_9$ and $C_{13}H_2O_5(OAc)_4$. The same acetyl derivative was obtained from galloflavin by Herzig and Pollak's method of acetylation (Abstr., 1901, i, 478).

The action of diazomethane on galloflavin suspended in ether leads to the formation of the *methyl* derivative, $C_{15}H_3O_5(OMe)_5$, which crystallises in yellow needles and melts at 235—237°.

Resoflavin, obtained by oxidation of 3:5-dihydroxybenzoic acid, yields an *acetyl* derivative, which melts at 274—277°, and, by the action of diazomethane, a yellow *methyl* derivative, which melts at 282—283°. Resoflavin and its derivatives closely resemble the galloflavin compounds. G. Y.

Ononin. III. FRANZ VON HEMMELMAYR (*Monatsh.*, 1904, 25, 555—582. Compare Abstr., 1902, i, 480; 1903, i, 508).—A molecular weight determination with ononetin shows that this substance has the formula $C_{18}H_{16}O_5$, which agrees with the formula $C_{25}H_{26}O_{11}$ for ononin.

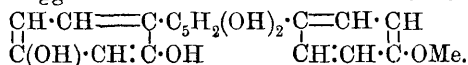
Ononetin is precipitated by carbon dioxide from its solution in aqueous baryta; it dissolves in aqueous ammonia to a green solution, from which it slowly separates. A small part dissolves in aqueous potassium hydroxide to a green solution from which hydrochloric acid precipitates a black tar. Formononetin dissolves with more or less difficulty in 8 per cent. aqueous potassium hydroxide, from which it is reprecipitated as a jelly by the addition of sulphuric acid. The oxidation of formononetin with potassium permanganate in alkaline solution leads to the formation of anisic acid and of two substances which melt at about 74° and 155° respectively, and are methoxy-

compounds. If only a small quantity of potassium permanganate is used in the oxidation, no anisic acid is formed, but a *substance* is obtained which yields a *hydrazone* melting at 213—214°.

The action of boiling nitric acid (1-acid : 3-water) on formononetin leads to the formation of a crystalline *substance* melting at 186°, a *mixture* of substances melting at 150—155°, and a trinitrodihydroxybenzene, which melts at 163° and is isomeric with styphnic acid; it yields a *silver* salt, $C_6HO_8N_3Ag_2$. The action of bromine on formononetin in alkaline solution leads to the formation of a mixture of *bromo*-derivatives, which melts between 242° and 261°, but if the bromination is carried out in glacial acetic acid solution in a sealed tube at 125°, the white, crystalline compound obtained melts at 325° and approximates in composition to the formula $C_{19}H_9O_5Br_5$. When the mixture of bromo-derivatives of formononetin is boiled with 10 per cent. aqueous potassium hydroxide, it yields a *product* which crystallises in glistening scales, melts at 175—176°, and has a composition between $C_{18}H_{16}O_5Br_4$ and $C_{18}H_{15}O_5Br_3$.

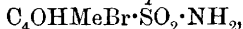
The action of bromine on ononetin in chloroform solution leads to the formation of a *substance* which crystallises in colourless prisms; one preparation melted at 133—134° and became a clear liquid at 145°; a second preparation melted at 142—150°. The composition of both preparations lies between $C_{18}H_{16}O_5Br_2$ and $C_{18}H_{13}O_5Br_3$.

The author suggests that ononetin has the constitution :

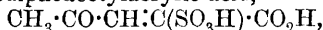


G. Y.

Sulphonamido-derivatives of Furan. HENRY B. HILL and J. P. SYLVESTER (*Amer. Chem. J.*, 1904, 32, 185—228).—*Potassium 3-sulpho-5-methylpyromucate*, $C_6H_4O_6SK_2 \cdot 2H_2O$, crystallises in slender prisms and becomes anhydrous at 130°. Phosphorus pentachloride, followed by ammonia, converts it into 3-sulphonamido-5-methylpyromucamide, $NH_2 \cdot SO_2 \cdot C_4OHMe \cdot CO \cdot NH_2$, which crystallises from water in prisms, melts at 196—197°, and dissolves readily in alcohol, sparingly in chloroform; its aqueous solution is neutral to litmus. Alkali hydroxides convert it in the cold into 3-sulphonamido-5-methylpyromucic acid, $C_6H_7O_5NS$, crystallising in rectangular prisms, melting at 217—218°, and dissolving readily in alcohol, sparingly in ether. The *potassium* salt contains H_2O , and the *barium* salt contains $3H_2O$; the *lead*, *calcium*, and *silver* salts are also described. Bromine oxidises solutions of the salts to 2-bromo-3-sulphonamido-5-methylfuran,



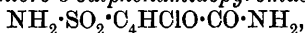
which crystallises from water in prisms, melts at 123°, and dissolves readily in alcohol or ether, sparingly in cold benzene or chloroform. Although neutral to litmus, it dissolves readily in dilute alkali hydroxides and is not decomposed on boiling. Acids precipitate it unchanged. Some sulphoacetylacrylic acid,



is formed during the oxidation, especially when the bromine is in excess.

Potassium 5-chloro-3-sulphopyromucate (Hill and Hendrixson,

Abstr., 1893, i, 313) reacts with phosphorus pentachloride and ammonia to form 5-chloro-3-sulphonamidopyromucamide,



which crystallises from water in thick prisms and melts at 212° . Barium hydroxide converts it into 5-chloro-3-sulphonamidopyromucic acid, crystallising in prisms, melting at 194 – 195° , and dissolving readily in alcohol, sparingly in ether. The *potassium*, *barium*, *calcium*, *lead*, and *silver* salts are described. Bromine oxidises the salts to 5-chloro-2-bromo-3-sulphonamidofuran, $\text{C}_4\text{H}_3\text{O}_3\text{NClBrS}$, which crystallises from water in long needles, melts at 134 – 135° , and dissolves very readily in alcohol, sparingly in chloroform or benzene. It is a weak acid and forms salts with alkalis.

The action of phosphorus pentachloride on potassium 5-bromopyromucate (Hill and Sanger, Abstr., 1886, 446) results in the replacement of the bromine in the nucleus by chlorine. Phosphorus pentabromide, however, followed by ammonia, reacts to form 5-bromo-3-sulphonamidopyromucamide, crystallising in prisms, melting at 219 – 220° , and dissolving sparingly in cold water or alcohol, readily on heating. Barium hydroxide hydrolyses it to 5-bromo-3-sulphonamidopyromucic acid, which melts at 190 – 191° and dissolves readily in water or alcohol. The *potassium*, *barium*, *lead*, and *silver* salts are described. Bromine forms 2:5-dibromo-3-sulphonamidofuran, crystallising in long prisms and melting at 153.5° . The *potassium* salt crystallises from alcohol in glistening scales.

The derivatives of 3-sulphonamidopyromucic acid described are not converted into sulphimides on heating alone or with dehydrating agents.
C. H. D.

Properties of Oxygen in the Pyran Ring. Dinaphthapyran (Dinaphthaxanthen) Series. ROBERT FOSSE (*Ann. Chim. Phys.*, 1904, [viii], 2, 233–284; 289–345).—A *résumé* of work already published (compare Abstr., 1901, i, 323, 384, 604, 643; 1902, i, 51, 171, 304, 368, 449, 689; 1903, i, 49, 357; this vol., i, 83, 519).

M. A. W.

Preparation of Indole. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 152683).—Indole may be prepared by heating phenylglycine or its derivatives, such as phenylglycine-*o*-carboxylic acid or its esters, anilides, amide, &c., with oxides or hydroxides of alkalis or alkaline earths. In the case of phenylglycine and its simpler derivatives, such as tolylglycine, it is also advisable to add sodium or sodamide. The addition of reducing agents, such as iron, sulphites, or sodium ethoxide, also improves the yield. The temperature should not rise above 300° , so that no distillation occurs. After dissolving in water, the indoxyl derivatives simultaneously formed are removed by oxidation, and the indole is extracted from the filtrate by means of ether or benzene, or by distillation with steam, and finally precipitating as picrate.

C. H. D.

Colouring Matters derived from Pyridine. II. W. KÖNIG (*J. pr. Chem.*, 1904, [ii], 70, 19–56. Compare this vol., i, 449; Zincke, this vol., i, 448).—The occurrence in two modifications and the

fluorescence of the colouring matters derived from pyridine by the action of the cyanogen bromide and a primary aromatic amine are now ascribed to desmotropism between the forms $\begin{array}{c} \text{CH:CH}\cdot\text{CH:NR} \\ \text{CH:CH}\cdot\text{NH}_2\text{RX} \end{array}$ and

$\begin{array}{c} \text{CH:CH}\cdot\text{CH}\cdot\text{NHR} \\ \text{CH:CH}\cdot\text{NHRX} \end{array}$. The first is the hydrohaloid of a dianilide of glutaconic aldehyde, the second is an arylaminoaryldihydropyridinium haloid.

The following compounds are described, the temperatures indicated being melting points.

Arylaminoaryldihydropyridinium Bromides.—From *p*-nitroaniline, $\text{R} = \text{C}_6\text{H}_4\cdot\text{NO}_2$, 149° ; from *m*-nitroaniline, 167° ; from *o*-toluidine, $\text{R} = \text{C}_6\text{H}_4\text{Me}$, 165° ; from *m*-toluidine, 143° ; from *p*-toluidine, 166° ; from *o*-anisidine, $\text{R} = \text{C}_6\text{H}_4\cdot\text{OMe}$, 148° ; from *p*-anisidine, 148 — 149° ; from *p*-aminodimethylaniline, $\text{R} = \text{C}_6\text{H}_4\cdot\text{NMe}_2$, 175° .

Of the nitroanilines, the para-compound combines most readily with pyridine and cyanogen bromide, forming the colouring matter, whilst this reaction takes place least readily with the ortho-isomeride; the product from the latter has not been purified.

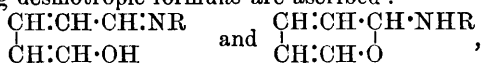
Arylpyridinium salts, $\text{CH} \begin{array}{c} \text{CH}\cdot\text{CH} \\ \text{CH:CH} \end{array} \text{NRCl}$, are obtained when the foregoing colouring matters are heated with hydrochloric acid at 140° or boiled with naphthalene or nitrobenzene. The colouring matters from the toluidines are decomposed when boiled with toluidine, whereas that from *p*-aminodimethylaniline yields the arylpyridinium bromide when boiled with chloroform.

The following arylpyridinium salts were prepared: From *p*-nitroaniline, $\text{R} = \text{C}_6\text{H}_4\cdot\text{NO}_2$: *ferrichloride*, 141° ; *aurichloride*, 269° ; *platinichloride*, 231° (with decomposition); *ferrichloride* of the bromide, 149° . From *m*-nitroaniline: *bromide*, 229 — 230° ; *ferrichloride* of the bromide, 163° ; *picrate*, 135° ; *dichromate*, 206° (with decomposition); *platinichloride*, 236° ; *aurichloride*, 233° . From *o*-toluidine, $\text{R} = \text{C}_6\text{H}_4\text{Me}$: *ferrichloride* of the bromide, 105° ; *platinichloride*, decomposes at 219° ; *picrate*, 132° . From *m*-toluidine: *ferrichloride* of the bromide, 101° ; *aurichloride*, 176° . From *p*-toluidine: *ferrichloride* of the bromide, 151 — 152° . From *p*-anisidine, $\text{R} = \text{C}_6\text{H}_4\cdot\text{OMe}$: *ferrichloride* of the bromide, 164° . From *p*-aminodimethylaniline, $\text{R} = \text{C}_6\text{H}_4\cdot\text{NMe}_2$: *dipicrate*, 139 — 140° .

The action of hydrochloric acid on the colouring matter from *p*-nitroaniline at 180° leads to the formation of 2:3:5:6-tetrachloroquinol. When acted on by bromine in boiling glacial acetic acid solution, the colouring matter from *p*-nitroaniline yields 2:6-dibromo-*p*-nitrophenylpyridinium perbromide, $\text{C}_6\text{H}_3\text{Br}_2(\text{NO}_2)\cdot\text{C}_5\text{H}_5\text{NBr}_3$, which crystallises in yellow plates and melts at 217 — 218° , and 2:6-dibromo-*p*-nitroaniline. 2:6-Dibromo-*p*-nitrophenylpyridinium bromide, obtained from the perbromide by the action of boiling acetone or acetic acid, crystallises in yellow plates and melts at 280° .

The action of sodium hydroxide on *p*-nitrophenylpyridinium chloride and on 2:6-dibromo-*p*-nitrophenylpyridinium bromide leads to the formation of red compounds, of which that derived from the dibromo-

compound crystallises in microscopic needles and melts at 165—166°. To these substances, which are analogous to those described by Zincke, the following desmotropic formulæ are ascribed :



where R is $\text{C}_6\text{H}_4\cdot\text{NO}_2$ or $\text{C}_6\text{H}_2\text{Br}_2\cdot\text{NO}_2$.

The supposed formation of a colouring matter from *o*-toluidine and 2-methylpyridine is found to have been due to the presence of pyridine. On the other hand, a colouring matter is formed with 3-methylpyridine. G. Y.

Influence of Oxides and Salts of Rare Elements on Skraup's Quinoline Synthesis. BENJAMIN M. MARGOSCHES (*J. pr. Chem.*, 1904, [ii], 70, 129—136).—The yield of quinoline in Skraup's synthesis is increased by the addition of commonly occurring metallic salts such as those of copper and iron. The condensation also takes place, but not to the same extent, if the nitrobenzene is replaced by the mixture of oxides or sulphates of the rare elements obtained from commercial cerium oxalate. G. Y.

Preparation of 2-Phenylquinoline. ERNST MURMANN (*Monatsh.*, 1904, 25, 621—631. Compare Abstr., 1892, 1003).—The author describes a series of quantitative experiments in the preparation of 2-phenylquinoline from cinnamaldehyde and aniline, using sulphuric or hydrochloric acid as the condensing, nitrobenzene, picric acid, or arsenic acid as the oxidising, agent. The best yield (31 per cent. of the calculated quantity of pure 2-phenylquinoline) was obtained by mixing aniline (93 parts), nitrobenzene (9 parts), and water (12 parts), cooling, and adding sulphuric acid (120 parts), and finally introducing 33 parts of the aldehyde, the mixture being well stirred and then heated at 135—142° for five hours. The author discusses the causes of the small yields in such syntheses. G. Y.

***as*-Phenylbenzylhydrazine.** RUDOLF OFNER (*Monatsh.*, 1904, 25, 593—602. Compare Philips, Abstr., 1889, 1159; Minunni, Abstr., 1893, i, 97).—*as*-Phenylbenzylhydrazine, freshly prepared from benzyl chloride and phenylhydrazine, contains 10—20 per cent. of phenylbenzylbenzylidenehydrazine (Philips, *loc. cit.*). The hydrazone is precipitated on adding cold alcohol, or when the hydrazine is dissolved in very dilute aqueous hydrochloric acid. If the hydrochloride of the hydrazine is precipitated by addition of concentrated hydrochloric acid and allowed to remain in contact with the mother liquor, it gradually changes into the hydrazone, the conversion being complete in 2—3 weeks. Free phenylbenzylhydrazine also changes, but more slowly, into phenylbenzylbenzylidenehydrazine; after five years, a specimen contained 45 per cent. of the latter substance. The change is accompanied by the formation of phenylhydrazine.

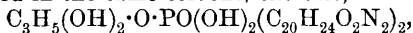
as-Phenylbenzylhydrazine, which has been rapidly purified by solution in very dilute hydrochloric acid, precipitation of the hydrochloride, and liberation of the base, is a colourless oil which boils at 216—218° under 38 mm. pressure. With benzaniline, phenylbenzylhydrazine forms phenylbenzylbenzylidenehydrazine and aniline.

Minunni's supposed semicarbazide of phenylbenzylhydrazine was the benzylidenehydrazine, as also was Philips' diphenyldibenzyltetrazone.

Paal and Bodewig's bisphenyl-*o*-nitrobenzylhydrazine (Abstr., 1892, 1455) was probably phenyl-*o*-nitrobenzyl-*o*-nitrobenzylidenehydrazine.

G. Y.

Quinine Glycerophosphates. P. CARRE (*Bull. Soc. chim.*, 1904, [iii], 31, 803—805).—When glyceryl dihydrogen phosphate (this vol., i, 133, 215) (1 mol.), dissolved in alcohol, is mixed with quinine (2 mols.) dissolved in the same solvent, the salt,



is formed and may be obtained in colourless needles by addition of ether (compare Adrian and Trillat, Abstr., 1898, i, 550). The salt is slightly soluble in water; the anhydrous form melts at 148.5° and is soluble in acetone, whereas the tetrahydrate begins to melt at 147.5° and is insoluble in acetone.

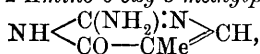
The salt, $\text{C}_3\text{H}_5(\text{OH})_2\cdot\text{O}\cdot\text{PO}(\text{OH})_2\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2$, similarly prepared, forms white needles, melts at 151 — 152° , and has solubilities similar to those of the preceding salt, the dihydrate being insoluble in acetone.

T. A. H.

Preparation of Hydroxyhydroquinine. VEREINIGTE CHININ-FABRIKEN ZIMMER & Co. (D.R.-P. 152174).—On dissolving quinine or its salts in cold concentrated sulphuric acid and diluting with water until the solution contains 20 per cent. of sulphuric acid and boiling, the soluble sulphonic acid at first formed is converted into hydroxyhydroquinine. Sodium hydroxide precipitates the base, which forms a bitter, white, crystalline powder, dissolving very sparingly in water or ether, readily in alcohol or acetone. The hydrochloride forms crystals containing $2\text{H}_2\text{O}$, becomes anhydrous at 100° , and darkens at 175° .

C. H. D.

Pyrimidines. Synthesis of 2-Amino-5-methyl-6-oxypyrimidine. TREAT B. JOHNSON and SAMUEL H. CLAPP (*Amer. Chem. J.*, 1904, 32, 130—145).—2-Amino-6-oxy-5-methylpyrimidine,



obtained by the condensation of guanidine with ethyl sodioformylpropionate, crystallises in prisms, melts and decomposes at 320 — 321° , and is soluble in water at 25° to the extent of 0.43 per cent.; it dissolves readily in sodium hydroxide solution, and is reprecipitated on neutralisation with carbon dioxide or dilute sulphuric acid. The hydrochloride, picrate, sulphate, and platinichloride are described.

α -Methyl- β -guanidineacrylic acid, formed as an intermediate product in the preparation of 2-amino-6-oxy-5-methylpyrimidine, is capable of existing in two modifications. trans- α -Methyl- β -guanidineacrylic acid,

$\text{CH}_3 \cdot \text{C} \cdot \text{CO}_2\text{H}$
 $\quad \quad \quad \parallel$
 $(\text{NH}_2)_2\text{C} \cdot \text{N} \cdot \text{CH}$, crystallises in prisms, melts and decomposes at 329 — 332° , is soluble in water at 25° to the extent of 0.08 per cent., and has both basic and acidic properties. When this acid is dissolved in 9 per cent. sodium hydroxide solution, it is converted into

2-amino-6-oxy-5-methylpyrimidine, but cold sodium hydroxide of 2 per cent. strength does not effect this change. *cis-a-Methyl-β-guanidine-acrylic acid*, $\text{CH}_3 \cdot \underset{\text{HC} \cdot \text{N} : \text{C}(\text{NH}_2)_2}{\overset{\text{C} \cdot \text{CO}_2\text{H}}{\text{C}}}$, crystallises in slender needles, melts at 319—320°, slowly decomposes at a higher temperature, and has a solubility in water at 25° of 0.84 per cent. This modification, unlike the *trans*-acid, cannot be reprecipitated from an alkaline solution, but is converted into the pyrimidine even by cold 2 per cent. sodium hydroxide.

By the condensation of ethyl formate with ethyl phthaliminoacetate in presence of sodium, ethyl sodioformylphthaliminoacetate is obtained. When a solution of this compound is acidified with hydrochloric acid, ethyl 4-hydroxyisocarbostyryl-3-carboxylate (Gabriel and Colman, *Abstr.*, 1900, i, 358) is produced. 5-Phthalimino-2-ethylthiol-6-oxy-pyrimidine, $\text{NH} \left\langle \underset{\text{CO} \cdot (\text{N} : \text{C}_8\text{H}_4\text{O}_2) \cdot \text{C}}{\overset{\text{C}(\text{SEt}) = \text{N}}{\text{C}}} \right\rangle \text{CH}$, prepared by the condensation of ψ -ethylthiocarbamide with ethyl sodioformylphthaliminoacetate, crystallises in rhombic plates and melts at 230—231°; when dilute hydrochloric or sulphuric acid is added to a solution of this compound in an alkali hydroxide, α -phthalimino- β - ψ -ethylthiocarbamidoacrylic acid, $\text{NH}_2 \cdot \text{C}(\text{SEt}) : \text{N} \cdot \text{CH} : \text{C}(\text{N} : \text{C}_8\text{H}_4\text{O}_2) \cdot \text{CO}_2\text{H}$, is precipitated, which crystallises from alcohol in small prisms, melts at 131°, and is decomposed at a higher temperature with formation of the pyrimidine.

5-Benzoylamino-2-ethylthiol-6-oxy-pyrimidine,



obtained by the action of ψ -ethylthiocarbamide on ethyl sodium hydroxymethylenhippurate, crystallises from alcohol in needles and melts at 238—239°; it is soluble in alkali hydroxides and is reprecipitated by hydrochloric acid. E. G.

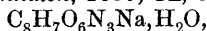
Uric Acid Group. Constitution of Murexide and of Several of the Derivatives of Uric Acid related to it. OSCAR PILOTY and KARL FINCKH (*Annalen*, 1900, 333, 22—71).—After a summary of the present view of the constitution of murexide, new methods of preparing this substance are described.

A solution of alloxantin (5 grams) in 200 c.c. of boiling water is poured into a solution of ammonium acetate (25 grams) in 100 c.c. of water at 80°, just alkaline with ammonia; murexide in a yield of 80 per cent. crystallises out; a small quantity of uramil separates afterwards. Excess of ammonia must be avoided, and the ammonium acetate cannot be replaced by another ammonium salt with advantage. The alloxantin may, however, be replaced by a mixture of ammonium dialurate and alloxan. These reactions account for the formation of murexide from uric acid and nitric acid and for the ordinary murexide test for uric acid, in both cases alloxantin being formed as an intermediate product.

Potassium purpurate can be very readily prepared by shaking up a solution of potassium uramil with an ethereal solution of iodine, the purpurate crystallising out during the process: $2\text{C}_4\text{H}_3\text{O}_3\text{N}_3\text{K}_2 + 2\text{I} +$

$\text{H}_2\text{O} = \text{C}_4\text{H}_4\text{O}_3\text{N}_5\text{K} + 2\text{KI} + \text{KOH} + \text{NH}_3$. In the presence of the excess of alkali, a portion of the uramil is oxidised to oxalic acid.

In agreement with Beilstein (*Annalen*, 1858, 107, 176), murexide is found to have the composition $\text{C}_8\text{H}_5\text{O}_6\text{N}_3\cdot\text{H}_2\text{O}$, the water of crystallisation being lost at 110° . In addition to the sodium salts previously described by Fritzsche (*Annalen*, 1839, 32, 316), a sodium salt,

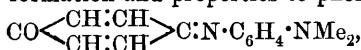


isomeric with Fritzsche's salt, was obtained by adding a saturated solution of sodium hydrogen carbonate to a solution of that salt, and forms slender, grass-green needles; when a solution of this salt is added to a little warm dilute sodium hydroxide, another sodium salt, $\text{C}_8\text{H}_3\text{O}_6\text{N}_5\text{Na}_2\cdot 3\text{H}_2\text{O}$, crystallises out in bright red needles.

The decomposition of murexide by acids yields alloxantin, uramil, and alloxan in varying proportions, as Liebig and Wöhler found; it is suggested that alloxantin is the primary product, which (as has been shown above) reacts with the ammonium chloride formed to give uramil and alloxan.

Since neither the degradation of murexide nor its synthetic formation from uramil and alloxan can be carried out in such a way as to throw light on its constitution, it was hoped to gain some information in the preparation of murexide-like substances from alloxan. A series of dyes has thus been synthesised; they are called the "ureïdes."

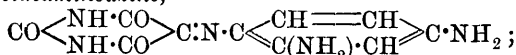
Dimethylureideindoaniline, $\text{CO} \begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{smallmatrix} \text{C:N}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, is prepared by mixing in alcoholic solution alloxan (1 mol.) and *as*-dimethyl-*p*-phenylenediamine (1 mol.), when small, dark blue crystals with a green reflex separate; it decomposes on heating, and is immediately converted by acids (even acetic acid) into alloxan and the diamine, and is reduced to a colourless base which is oxidised by the air in the presence of alkalis. *Tetramethylureideindoaniline*, prepared from 1:3-dimethylalloxan and *as*-dimethyl-*p*-phenylenediamine, the two substances being mixed in chloroform solution, forms blue prisms with a green reflex and melts at 168° ; it is immediately decomposed into its components by acids and alkalis, and is reduced by zinc dust and acetic acid to a colourless, amorphous base, the *platinichloride* of which has been obtained as orange-yellow needles. In a similar manner, *p*-aminophenol can be substituted for the diamine, ureideindophenols being formed; similar substances are produced when dimethyl-ordibrom-alloxan is used. The constitution represented by the above formula is assigned to these compounds from the analogy which they show both in method of formation and properties to phenylindophenol,



which is produced by condensation of quinone and *as*-dimethyl-*p*-phenylenediamine, is immediately decomposed into its components by acids, and is insoluble in alkali hydroxides. It is suggested that in this condensation alloxan behaves as if it had a quinonoid structure.

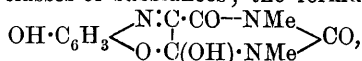
Since quinoneoxime, that is, nitrosophenol, condenses with phenols, it was thought that the similarly constituted alloxan derivative,

violuric acid, would be capable of a similar reaction; violuric acid will not react with phenols, but condenses with *m*-phenylenediamine, forming *ureideaminooxazine*,



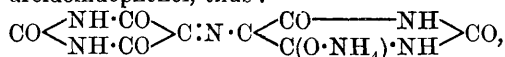
this substance is prepared by adding a solution of sodium hydroxide to a mixture of violuric acid and *m*-phenylenediamine hydrochloride, and separates as a brick-red, insoluble crystalline powder, which dissolves in sodium hydroxide, being converted into the *sodium* salt, $\text{C}_{10}\text{H}_6\text{O}_2\text{N}_5\text{Na} \cdot \frac{1}{2}\text{H}_2\text{O}$, which forms slender, golden-yellow needles. Dimethylvioluric acid and *m* phenylenediamine produce the *compound* $\text{C}_{10}\text{H}_5\text{O}_2\text{N}_5\text{Me}_2$, which can be crystallised from concentrated hydrochloric acid in yellow needles, soluble in sulphuric acid with a cherry-red coloration, and decomposing on heating. From these observations, the inference is drawn that violuric acid is the oxime of a substance of a quinonoid nature.

Alloxan and 1-amino-2:4-dihydroxybenzene condense to form the ureideoxazones, the alloxan again behaving as a quinone, thus, dimethylalloxan and aminoresorcinol, when mixed in alcoholic solution, yield a *compound*, $\text{C}_{12}\text{H}_{11}\text{O}_5\text{N}_3 \cdot \text{H}_2\text{O}$, which forms a reddish-brown powder decomposing at a high temperature, and can be boiled with acids; the solutions of the salts are dark blue, the solution in sulphuric acid has the colour of permanganate. *Ureidehydroxyoxazone*, prepared from alloxan and aminoresorcinol, was isolated in the form of the *barium* salt, $\text{C}_{10}\text{H}_6\text{O}_5\text{N}_3\text{Ba} \cdot 2\text{H}_2\text{O}$, which is an amorphous, dark blue precipitate. The great stability of these ureidehydroxyoxazones offers a marked contrast to the ureideindophenyl compounds; further, a comparison of the properties of this class with those of the hydroxydinaphtha-oxazones points to a close resemblance between the constitution of these two classes of substances; the formula



resembling that of the naphtha-oxazone, is therefore suggested.

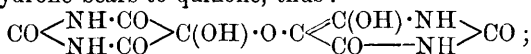
From the results above described, it might be concluded that murexide was a ureideindophenol, thus:



but the stability of murexide and the ease of its formation are opposed to this view; it seems more probable that it is a ureidehydroxyoxazone, $\text{NH} \cdot \text{CO} \cdot \text{C} \equiv \text{N} \cdot \text{C} \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}(\text{O} \cdot \text{NH}_4) \cdot \text{O} \cdot \text{C} \cdot \text{NH} \cdot \text{CO}$, a constitution which would account for its formation from uramil and alloxan and for its decomposition into alloxan, dialuric acid, and ammonia on the one hand (the alloxan and dialuric acid recombine to form the alloxantin), and into alloxan, uramil, and ammonia on the other; thus, $\text{C}_8\text{H}_8\text{O}_6\text{N}_3 + 2\text{H}_2\text{O} + 2\text{HCl} = \text{C}_4\text{H}_2\text{O}_4\text{N}_2 + \text{C}_4\text{H}_2\text{O}_2\text{N}_2(\text{OH})_2 + 2\text{NH}_4\text{Cl}$ and $\text{C}_8\text{H}_8\text{O}_6\text{N}_3 + \text{H}_2\text{O} + \text{HCl} = \text{C}_4\text{H}_2\text{O}_4\text{N}_2 + \text{C}_4\text{H}_2\text{O}_2\text{N}_2(\text{OH}) \cdot \text{NH}_2 + \text{NH}_4\text{Cl}$. The want of stability of murexide towards acids is a difficulty in the way of this view, but it is pointed out that the benzene ring confers stability on the oxazone ring, and that in murexide this ring is linked with a ureide ring, a

fact which probably accounts for the instability towards acids. For murexide is suggested the name *ammonium diureideoxazonate*.

A consideration of the properties of alloxantin shows that the formula at present accepted, $\left[\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} \text{C}(\text{OH}) \cdot \right]_3$, is unsatisfactory; for example, alloxantin does not form stable salts, and is decomposed by dilute and cold solutions of alkalis into salts of alloxan and dialuric acid, the same decomposition being even effected by ammonium chloride and dimethylamine acetate; moreover, hydroxylamine converts this substance into the oxime of alloxan, violuric acid; a mixture of mol. quantities of alloxan and ammonium dialurate, which in these circumstances yields no alloxantin, produces as much murexide as the equivalent quantity of alloxantin. It appears, therefore, as if the components of alloxantin, dialuric acid, and alloxan were already present in very loose combination. This relation is best expressed by supposing that alloxantin bears to alloxan the relation that quinhydrone bears to quinone, thus:



a comparison of the properties of quinhydrone and alloxantin confirms this view, and, further, a comparison of the properties of alloxan and quinone shows that they have a similar chemical behaviour; they act as oxidising agents, yield dyes, colour the skin, combine, on the one hand, with dialuric acid, and, on the other hand, with quinol, producing similar substances, alloxantin and quinhydrone, and are reduced respectively by hydrochloric and hydrobromic acids to alloxantin and quinhydrone.

When alloxantin in aqueous solution is treated with excess of a methylamine acetate solution, 7-methyluramil crystallises from the deep violet solution. 7-Ethyluramil, $\text{C}_4\text{H}_4\text{O}_3\text{N}_3\text{Et}$, is formed when ethylamine is substituted for methylamine, and crystallises in lustrous plates or slender needles. With dimethylamine, the coloration produced is not so marked, and no compound could be isolated on concentration.

7-Ethyluramil and alloxan react in the presence of ammonium carbonate, giving a deep purple-red solution from which murexide separates.

Alloxan and methyl- and ethyl-amines yield deeply-coloured solutions from which the corresponding purpurates of methylamine and ethylamine separate; a substituted murexide is not produced. When glycine is used instead of the base, a deeply-coloured solution is obtained from which the *glycine* salt of purpuric acid,



crystallises out in dark red, prismatic leaflets with a green reflex; it is decomposed by water and converted by treatment with a solution of ammonium chloride into murexide, glycine hydrochloride being at the same time formed. If the glycine and the alloxan are allowed to react at a higher temperature, the purpurate first formed is decomposed, and an amorphous substance, which is soluble in alkalis, is produced together with a compound, $\text{C}_6\text{H}_7\text{O}_5\text{N}_3 \cdot \text{H}_2\text{O}$; the latter crystallises in yellow needles, gives a blue alloxan reaction with ferrous sulphate, and is possibly uramilacetic acid.

K. J. P. O.

Preparation of 3':8-Dichlorocaffeine. C. F. BOEHRINGER & SÖHNE (D.R.-P. 151190. Compare D.R.-P. 105050).—3':8-Dichlorocaffeine is most readily prepared by passing a rapid stream of chlorine into fused 8-chlorocaffeine at 200°, the temperature being gradually lowered to 170°. At 150—160°, some 7':8-dichlorocaffeine is also produced. C. H. D.

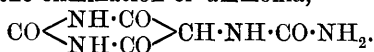
Action of Hydroxylamine and of Hydrazine on β -Alkyloxy- and β -Phenoxy-ethylenic Ketones. CHARLES MOUREU and M. BRACHIN (*Compt. rend.*, 1904, 139, 294—297).—The β -alkyloxy- and β -phenoxy-ethylenic ketones, $\text{OR}''\cdot\text{CR}:\text{CH}\cdot\text{COR}'$ (compare this vol., i, 811), react with hydroxylamine to form isooxazoles identical with those obtained by the action of hydroxylamine on the acetylenic ketones (compare this vol., i, 95), thus, 5-phenyl-3-ethylisooxazole was obtained from β -propionyl- α -ethoxystyrene, and 5-phenyl-3-propylisooxazole from β -butyryl- α -phoxystyrene. The reaction probably takes place in two stages: (1) the formation of the oxime, $\text{OR}''\cdot\text{CR}:\text{CH}\cdot\text{CR}'\cdot\text{NOH}$; (2) the elimination of one mol. of alcohol or phenol to form the isooxazole, $\text{O} \begin{smallmatrix} \text{N}=\text{CR}' \\ \text{CR}:\text{CH} \end{smallmatrix}$. By a similar reaction, β -alkyloxy- and β -phenoxy-ethylenic ketones yield pyrazoles on treatment with hydrazine, identical with those obtained by the action of hydrazine on the corresponding acetylenic ketones (compare Abstr., 1903, i, 581). 5-Phenyl-3-ethylpyrazole, $\text{NH} \begin{smallmatrix} \text{N}=\text{C}^{\text{Et}} \\ \text{CPh}:\text{CH} \end{smallmatrix}$, boils at 205—207° (corr.) under 17 mm. pressure, crystallises from light petroleum in colourless prisms melting at 82°, and forms a *picrate* crystallising in thin, prismatic needles, melting at 146°, on Maquenne's metal block. 5-Phenyl-3-propylpyrazole, $\text{NH} \begin{smallmatrix} \text{N}=\text{C}^{\text{Pr}} \\ \text{CPh}:\text{CH} \end{smallmatrix}$, boils at 212—215° under 20 mm. pressure and melts at 68°, its *picrate* crystallises in rhomboidal plates and melts at 105° on Maquenne's metal block. M. A. W.

Uramil. OSCAR PILOTY and CARL FINCKH (*Annalen*, 1904, 333, 71—99. Compare this vol., i, 820).—Uramil is very simply prepared by heating ammonium dialurate, closed vessels being employed to avoid oxidation.

Potassium uramil, $\text{CO} \begin{smallmatrix} \text{NK}\cdot\text{CO} \\ \text{NK}\cdot\text{CO} \end{smallmatrix} \text{CH}\cdot\text{NH}_2\cdot 2\text{H}_2\text{O}$, is obtained as slender, pale yellow needles by dissolving uramil in 50 per cent. warm potassium hydroxide, when partial decomposition takes place; the salt cannot be recrystallised without loss of potassium, and when exposed to moist air becomes intensely red, ammonia being evolved. Iodine converts the salt into potassium murexide, methyl iodide into 1:3-dimethyluramil (Techow, Abstr., 1895, i, 83). Of the salts of the form, $\text{CO} \begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \text{NM}\cdot\text{CO} \end{smallmatrix} \text{CH}\cdot\text{NH}_2$, only the *barium* and *lead* salts have been prepared; the former is obtained by adding barium chloride to a solution of uramil in ammonia, and the latter as needles which readily become

rose-coloured in the air. The *acid potassium* salt, $C_4H_5O_3N_3, C_4H_4O_3N_3K$, is prepared by dissolving uramil in boiling dilute potassium hydroxide and crystallises in colourless, sparsely soluble leaflets which rapidly become red in the air; the sodium salt closely resembles the potassium salt.

When boiled with ten per cent. alkali hydroxide for several hours, uramil is decomposed, carbamide and aminomalonic acid being formed; further, the carbamide combines with the unchanged uramil, forming ψ -uric acid, with the elimination of ammonia,



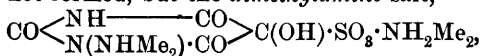
The ψ -uric acid is in its turn hydrolysed into carbamide and *carbamido-malonic acid*, $NH_2 \cdot CO \cdot NH \cdot CH(CO_2H)_2$. From the product of the reaction, *potassium ψ -urate*, $C_5H_5O_4N_4K, H_2O$, crystallises; the filtrate is evaporated and alcohol added, when the potassium salts of aminomalonic and carbamidomalonic acids separate as an oil, from which the potassium aminomalonate slowly crystallises. The carbamidomalonic acid is purified by converting the oily potassium salt into the lead salt, from which the free acid can be prepared; it forms prisms melting and decomposing at $148-150^\circ$; it is decomposed by boiling with water, hydantoic acid (melting and decomposing at 155°) being formed; the *potassium* salt is extremely soluble, the *ammonium* salt, $C_4H_4O_5N_2(NH_4)_2, H_2O$, crystallises in soluble needles, the *barium* salt crystallises in lustrous prisms with $2H_2O$, and the *lead* salt with H_2O in prisms, and the *silver* salt in anhydrous prisms.

It has been ascertained that the "*uramilic acid*," $C_{10}H_{20}O_{15}N_{10}$, described by Liebig and Wöhler (*Annalen*, 1838, 26, 314) as being formed by the action of dilute sulphuric acid on uramil, is the *acid ammonium* salt of hydurilic acid (Schlieper, *Annalen*, 1845, 56, 11; and Bayer, *ibid.*, 1864, 132, 302).

7-Acetyluramil, which can be easily purified by conversion into the ammonium salt, is hydrolysed by boiling with water and forms a series of salts; the *potassium* salt, $C_6H_6O_4N_3K$, crystallises in rhombic prisms, and the *ammonium* and *silver* salts in slender needles; the *barium*, *lead*, and *copper* salts are all crystalline.

When dipotassium uramil is oxidised in aqueous solution in the cold, a crystalline *potassium* salt, $C_4H_4O_4N_3K, \frac{1}{2}H_2O$, can be isolated; on acidifying this salt, carbon dioxide is evolved, and acid potassium alloxanate can be isolated from the product. On treating the alkaline solution of the salt, ammonia is evolved and normal potassium alloxanate formed. The potassium salt is isomeric with potassium oxonate, obtained by oxidising uric acid (Medicus, *Annalen*, 1875, 175, 232). It is suggested that this new acid is *aminohydantoincarboxylic acid*, $CO < \begin{matrix} NH \cdot CO \\ NH \cdot C(NH_2) \cdot CO_2H \end{matrix} >$. Attempts to obtain a similar compound by oxidising ψ -uric acid led only to the formation of alloxanic acid.

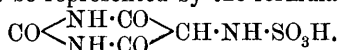
When alloxan is treated in aqueous solution with a neutral solution of dimethylamine sulphite, the expected dimethylamine dimethylthionurate is not formed, but the *dimethylamine* salt,



which is obtained as needles or prismatic crystals on evaporating the product of the reaction; exposed to the air, the compound becomes rose-coloured, and when heated at 120° dimethylamine is given off and the substance assumes the colour of murexide. When the solution is boiled, it becomes pale red, but little decomposition occurs; on heating the concentrated aqueous solution under pressure at 140° , complete decomposition takes place, carbon dioxide, sulphur dioxide, ammonia, dimethylamine, and sulphuric acid being produced. When warmed with dilute acids, sulphur dioxide is evolved and alloxantin and dimethylamine produced; no trace of substituted uramil was discovered.

The *potassium* salt, $C_4H_2O_7N_2SK_2 \cdot H_2O$, prepared from the dimethylamine salt, crystallises in prisms, and the *ammonium* salt, which is anhydrous, in sparingly soluble plates; the *barium* salt crystallises in needles with $2H_2O$, and the *lead* salt in nodular aggregates.

The constitution of the sulphite additive compounds of alloxan is discussed in the light of these results, and it is concluded that thionuric acid must be represented by the formula

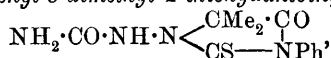


K. J. P. O.

Action of Carbimides and Thiocarbimides on Hydrazoacids. JAMES R. BAILEY (*J. Amer. Chem. Soc.*, 1904, 26, 1006—1026). —[With SALOMON F. ACREE and P. T. MILLER.]—1-Carbamido-3-phenyl-

5-methyl-2-thiohydantoin, $NH_2 \cdot CO \cdot NH \cdot N < \begin{array}{c} CHMe \cdot CO \\ CS - NPh \end{array}$, prepared by boiling an alcoholic mixture of phenylthiocarbimide and ethyl semicarbazinopropionate for half an hour, crystallises from methyl alcohol in aggregates of short, colourless prisms and melts and decomposes at 206° . The analogous 1-carbamido-5-methyl-3-allyl-2-thiohydantoin, prepared by using allylthiocarbimide, melts at 167° . 1-Carbamido-5-methyl-3-ethyl-2-thiohydantoin crystallises from alcohol and melts at 153° .

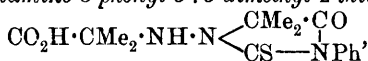
1-Carbamido-3-phenyl-5-dimethyl-2-thiohydantoin,



obtained by boiling a solution of ethyl semicarbazinoisobutyrate and phenylthiocarbimide in ethyl acetate, decomposes at 191° .

1-Amino-3-phenyl-5-methyl-2-thiohydantoin, prepared by heating 1-carbamido-3-phenyl-5-methyl-2-thiohydantoin with concentrated hydrochloric acid for 1 hour at 120° , crystallises from water or alcohol in long, slender, pointed prisms, melts at 150° , and combines with phenylthiocarbimide to form a *thiocarbamide* decomposing at 223° . 1-Amino-3-phenyl-5-dimethyl-2-thiohydantoin, prepared similarly, crystallises from alcohol in long needles, melts at 173° , and with a boiling acetic acid solution of phenylthiocarbimide gives the crystalline derivative, $C_{18}H_{13}ON_4S_2$, which decomposes at 233° ; the *benzylidene* derivative, $C_{18}H_{17}ON_3S$, of the amino-compound crystallises from alcohol and melts at 135° .

When 1-carbamido-3-phenyl-5-methyl-2-thiohydantoin is heated with aqueous barium hydroxide at 65°, it is probably first hydrolysed to the compound $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{N}(\text{CHMe} \cdot \text{CO}_2\text{H}) \cdot \text{C}(\text{SH}) \cdot \text{NPh}$, which, by loss of NH_3 , gives 2-phenylimino-5-hydroxy-2:3-dihydro-1:3:4-thio-diazole-3-propionic acid, $\text{CO}_2\text{H} \cdot \text{CHMe} \cdot \text{N} \begin{smallmatrix} \text{C}(\text{NPh}) \cdot \text{S} \\ \text{N} = \text{C} \cdot \text{OH} \end{smallmatrix}$; this crystallises from water in clusters of radiating needles, melts and decomposes at 220°, and can be titrated with sodium hydroxide as a dibasic acid; its ethyl ester $\text{C}_{13}\text{H}_{15}\text{O}_3\text{N}_3\text{S}$, crystallises from alcohol or benzene, melts at 171°, and gives a benzoyl derivative, $\text{C}_{20}\text{H}_{19}\text{O}_4\text{N}_3\text{S}$, crystallising in thin plates and melting at 110°. The amide, $\text{C}_{11}\text{H}_{12}\text{O}_2\text{N}_2\text{S}$, of the acid, crystallises from alcohol and melts and decomposes at 228°. 1-Carboxyisopropylamino-3-phenyl-5:5-dimethyl-2-thiohydantoin,



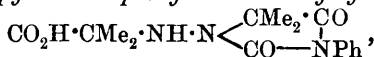
prepared by heating hydrazoisobutyric acid and phenylthiocarbimide with boiling glacial acetic acid, crystallises from benzene and ether, melts at 153°, and is hydrolysed by hydrochloric acid at 140–160°, giving 1-amino-3-phenyl-5:5-dimethyl-2-thiohydantoin (*supra*), a fact which confirms its structure. The nitroso-derivative, $\text{C}_{15}\text{H}_{18}\text{O}_4\text{N}_4\text{S}$, of the foregoing amino-compound crystallises from a mixture of benzene and light petroleum and melts and decomposes at 166°. The methyl ester, $\text{C}_{16}\text{H}_{21}\text{O}_3\text{N}_3\text{S}$, melts at 142°; the ethyl ester, $\text{C}_{17}\text{H}_{23}\text{O}_3\text{N}_3\text{S}$, melts at 84°.

1-Carboxyisopropylamino-5:5-dimethyl-3-allyl-2-thiohydantoin crystallises from benzene and melts at 121°; the analogous 3-ethyl derivative melts at 110°, and the 3-methyl compound at 129°. 1-Phenylamino-3-phenyl-5:5-dimethyl-2-thiohydantoin, $\text{NHPh} \cdot \text{N} \begin{smallmatrix} \text{CMe}_2 \cdot \text{CO} \\ \text{CS} - \text{NPh} \end{smallmatrix}$, prepared from phenylhydrazoisobutyric acid and phenylthiocarbimide, crystallises from benzene and melts at 206°. 1-Phenylamino-5:5-dimethyl-3-ethyl-2-thiohydantoin, obtained by using ethylthiocarbimide, melts at 85°.

α -Carbamido- $\alpha\beta$ -diphenylcarbamide, $\text{NHPh} \cdot \text{CO} \cdot \text{NPh} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, prepared by boiling a benzene solution of phenylsemicarbazide and phenylcarbimide, crystallises from alcohol and melts and decomposes at 210°. When phenylcarbimide is boiled in benzene solution with ethyl semicarbazinopropionate, the additive compound,

$\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{N}(\text{CO} \cdot \text{NHPh}) \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$, melting at 163°, is obtained. On boiling this with water, 1-carbamino-3-phenyl-5-methylhydantoin, $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{N} \begin{smallmatrix} \text{CHMe} \cdot \text{CO} \\ \text{CO} - \text{NPh} \end{smallmatrix}$, is formed; it crystallises from ethyl acetate in long, slender needles and melts and decomposes at 219°.

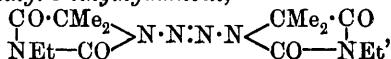
1-Carboxyisopropylamino-3-phenyl-5:5-dimethylhydantoin,



obtained by desulphurising the corresponding thiohydantoin with mercuric oxide or by the action of phenylcarbimide on hydrazoisobutyric acid, crystallises from alcohol in characteristic prisms, melts

at 205°, and can be titrated as a monobasic acid; the *ethyl* ester crystallises from ether in large, hexagonal prisms and melts at 98°. 1-Carboxyisopropylamino-3:5:5-trimethylhydantoin, prepared from the corresponding thio-compound, crystallises from water in slender prisms and melts at 169°. 1-Carboxyisopropylamino-5:5-dimethyl-3-ethylhydantoin melts at 140°. The corresponding 3-*allyl*-derivative melts at 114°.

1-Azo-5:5-dimethyl-3-ethylhydantoin,



obtained by the action of bromine water on 1-carboxyisopropylamino-5:5-dimethyl-3-ethylhydantoin in alcoholic solution, crystallises from alcohol and melts and decomposes at 234°. 1-Azo-3:5:5-trimethylhydantoin decomposes at 278° and 1-azo-3-phenyl-5:5-dimethylhydantoin at 270°. W. A. D.

1:2:3-Thiodiazoles. LUDWIG WOLFF [with H. KOPITZSCH and A. HALL] (*Annalen*, 1904, 333, 1—21. Compare Abstr., 1903, i, 203).—

The cyclic diazoanhydrides, $\begin{array}{c} \text{CR} : \text{CR}' \\ \text{N} = \text{N} \end{array} > \text{O}$, are converted by treatment

with ammonium sulphide into thiodiazoles, $\begin{array}{c} \text{CR} : \text{CR}' \\ \text{N} = \text{N} \end{array} > \text{S}$, which are more

stable than the compounds from which they are produced, not being attacked by mineral acids, and only slowly decomposed by boiling alcoholic alkali hydroxides; the substituted thiodiazoles are still more stable towards alkalis. They are very feeble bases, and their hydrochlorides yield double salts with mercury, gold, and silver salts. They combine with methyl iodide, and the resulting compounds yield strong bases on treatment with silver hydroxide.

The thiodiazoles are prepared by passing a current of hydrogen sulphide through an alcoholic solution of the diazoanhydride containing a small quantity of ammonium sulphide for 20—24 hours at 0—5°.

Ethyl 5-phenyl-1:2:3-thiodiazole-4-carboxylate, $\begin{array}{c} \text{C}(\text{CO}_2\text{Et}) : \text{CPh} \\ \text{N} = \text{N} \end{array} > \text{S}$,

prepared from the diazoanhydride of ethyl benzoylacetate, crystallises in colourless needles or plates melting at 42°, and on hydrolysis with sodium hydroxide yields the corresponding *acid*, which crystallises in colourless needles or leaflets melting with evolution of carbon dioxide at 157°, and becomes coloured when exposed to light. *Ethyl 5-methyl-1:2:3-*

thiodiazole-4-carboxylate, $\begin{array}{c} \text{C}(\text{CO}_2\text{Et}) : \text{CMe} \\ \text{N} = \text{N} \end{array} > \text{S}$, prepared from the diazo-

anhydride of ethyl acetoacetate, crystallises in needles or plates melting at 35°, and the corresponding acid (with H₂O) in needles, which melt at 74—75° and when anhydrous at 113°; it decomposes with evolution of carbon dioxide at 160°. When oxidised in alkaline solution with potassium permanganate, it is converted into 1:2:3-thiodiazole-4:5-di-

carboxylic acid, $\begin{array}{c} \text{C}(\text{CO}_2\text{H}) : \text{C}(\text{CO}_2\text{H}) \\ \text{N} = \text{N} \end{array} > \text{S}, \text{H}_2\text{O}$, which is isolated by extracting with ether and recrystallising from water containing hydrochloric

acid, when it forms colourless needles melting with evolution of carbon dioxide and formation of thiodiazole-4-carboxylic acid (m. p. 227°). The anhydrous acid melts at about 110° and is hygroscopic. This acid can also be prepared from the diazoanhydride from ethyl oxaloacetate. 1 : 2 : 3-*Thiodiazole-4-carboxylic acid*, prepared by boiling a solution of the dibasic acid just mentioned, crystallises from water, in which it is insoluble, in anhydrous prisms, decomposing at 228°.

5-*Phenyl-1:2:3-thiodiazole*, $\begin{matrix} \text{CH:CPh} \\ \text{N}=\text{N} \end{matrix} > \text{S}$, is prepared by heating small portions of the phenylthiodiazolecarboxylic acid at 160—170° and distilling the product with steam; it crystallises in prisms melting at 53—53·5°, and has an odour resembling that of nitrobenzene; this substance is very stable and is only very slowly decomposed by tin and hydrochloric acid; by a mixture of sulphuric and nitric acids, it is nitrated; the *additive* compound with mercuric chloride,

$\text{C}_8\text{H}_6\text{N}_2\text{S}, \text{HgCl}_2$, crystallises in long needles, becoming coloured at 160° and melting at 167°. The *methiodide*, $\text{C}_8\text{H}_6\text{N}_2\text{S}, \text{MeI}, \text{H}_2\text{O}$, prepared by heating the base with excess of methyl iodide at 110—120° for eight hours, crystallises in pale yellow needles melting and evolving gas at 136°, then solidifying again to melt at 158°; the anhydrous substance melts at 158° and is hygroscopic; the *methochloride* forms colourless needles, and the *platinichloride* yellowish-red needles melting at 151°; the *aurichloride* crystallises in sparsely yellow prisms melting at 180°.

5-*Methyl-1:2:3-thiodiazole*, prepared by heating 1 : 2 : 3-methylthiodiazole-4-carboxylic acid at 185° and distilling the product under reduced pressure, is a clear liquid of pleasant odour, which does not solidify at -18°, boils at 91° under 38 mm., at 88—89° under 34 mm., and at 184° under 755 mm. pressure; it has a sp. gr. 1·2363 at 0°, distils readily with steam, and becomes coloured when exposed to light. The *compound* with mercuric chloride crystallises in prisms; the *hydrochloride* forms hygroscopic needles, and the *aurichloride* yellow needles decomposing at 145°. The *methiodide*, $\text{C}_3\text{H}_4\text{N}_2\text{S}, \text{MeI}$, crystallises in pale yellow, hygroscopic needles melting at 76—77°; the *methochloride* forms colourless, hygroscopic needles, which yield a double salt with mercuric chloride, crystallising in prisms; the *platinichloride*,

$(\text{C}_3\text{H}_4\text{N}_2\text{S}, \text{MeCl})_2\text{PtCl}_4$, crystallises in orange-red needles or prisms melting and decomposing at 212°, and the *aurichloride* in yellow, lustrous leaflets melting at 136—137°. By treatment of the aqueous solution of the methiodide with moist silver oxide, a strongly alkaline solution of the free base can be prepared.

1 : 2 : 3-*Thiodiazole*, $\begin{matrix} \text{CH:CH} \\ \text{N}=\text{N} \end{matrix} > \text{S}$, is prepared by distilling thiodiazole-carboxylic or -dicarboxylic acid at 230—260° and distilling the resulting oil with steam; it is a clear oil with a pleasant odour, not solidifying at -19°, and boiling at 83—85° under 60 mm. and at 157° under 742 mm. pressure; it has a sp. gr. 1·3202 at 0°, and it is very stable towards acids, although easily decomposed with evolution of nitrogen by alkali hydroxides; with silver nitrate, it gives an amorphous and

with mercuric chloride a crystalline precipitate; the *hydrochloride* crystallises in colourless, hygroscopic needles or prisms melting at 70° , and sublimable; the *salt*, $C_2H_2N_2S, AuCl_3$, crystallises in pale yellow needles which become dark at 152° and are molten at 165° ; when crystallised from concentrated hydrochloric acid, the *aurichloride*, $C_2H_2N_2S, HCl, AuCl_3$, is obtained, crystallising in yellow needles decomposing at $150-160^{\circ}$. The *methiodide*, $C_2H_2N_2S, MeI$, is prepared in the usual manner, and crystallises in yellow prisms, which, when rapidly heated, melt and decompose at 222° , but when slowly heated become coloured at 210° and volatilise at 220° . When the aqueous solution is made alkaline, a bluish-green coloration appears, which rapidly becomes reddish-brown, nitrogen being evolved. An aqueous solution of the free base can be prepared. The *methochloride* crystallises in colourless, hygroscopic plates, decomposing into its components at 192° ; the double *salt* with mercuric chloride crystallises in prisms melting at $170-171^{\circ}$; the *aurichloride* crystallises in yellow needles decomposing at 252° ; the *platinichloride* crystallises in orange-red prisms which melt and evolve gas at 207° .

K. J. P. O.

Methyl Anthranilate; its Detection of Some Derivatives.

PAUL FREUNDLER (*Bull. Soc. chim.*, 1904, [iii], 31, 882-884).—*Methyl anthranilate picrate*, obtained by mixing alcoholic solutions of the two components, forms yellow needles, melts at $103.5-104^{\circ}$, and is readily soluble in alcohol.

When molecular quantities of methyl anthranilate and phenylthiocarbimide are warmed together at 100° , the 4-keto-2-thio-3-phenyl-tetrahydroquinazoline described by McCoy (*Abstr.*, 1897, i, 490) is formed.

The latter reaction may be employed for the detection and estimation of methyl anthranilate in the absence of other esters of this acid. The ester is isolated by steam distillation in presence of sodium carbonate and extraction with ether. The oil left on distilling off the solvent is mixed with excess of phenylthiocarbimide and heated at $100-120^{\circ}$ for 3-4 hours. The residue is then disintegrated by boiling with alcohol, and, when quite cold, the insoluble portion is filtered off and dried at $100-120^{\circ}$, the yield being approximately 98 per cent. of the theoretical.

The author has confirmed by this method the observation of Schmidt and V. Meyer, that methyl anthranilate is formed when isatoic anhydride is heated with methyl alcohol in closed tubes at 150° (*Abstr.*, 1887, 371). The yield of the ester in this reaction is equal to 28 per cent. of the anhydride used.

T. A. H.

Phenylmalononitrile. JOHN C. HESSLER (*Amer. Chem. J.*, 1904, 32, 119-130).—*Ethyl phenylcyanoacetate*, $C_6H_5 \cdot CH(CN) \cdot CO_2Et$, obtained by the condensation of phenylacetonitrile with ethyl carbonate, is a colourless oil which boils at 165.5° under 20 mm. and at 275° under the ordinary pressure, has a sp. gr. 1.09 at 22° , and is readily soluble in organic solvents but insoluble in water. When the ester is dissolved in aqueous solutions of alkali hydroxides, it gradually undergoes hydrolysis, forming phenylecyanoacetic acid; its solution in

aqueous ammonia slowly deposits crystals of the amide. The *sodium* derivative of the ester was obtained as a white, hygroscopic powder. *Phenylcyanoacetic acid* is a crystalline substance which melts at 92° and is soluble in water, alcohol, ether, or hot benzene; when heated at 150 — 160° , it undergoes decomposition with the formation of carbon dioxide and phenylacetoneitrile. The *amide* separates from an alcoholic solution in large crystals, melts at 147° , and is sparingly soluble in ether or cold water.

Ethyl phenylbenzylcyanoacetate, obtained by heating ethyl phenylcyanoacetate with benzyl chloride and sodium ethoxide, is a viscid, colourless liquid which boils at 231 — 233° under 32 mm. and at 216 — 217° under 16 mm. pressure, is insoluble in water, and is not affected by aqueous alkali hydroxide; it has a sp. gr. 1.13 at 22° .

Phenylmalononitrile, prepared by the action of phosphorus pentachloride on phenylcyanoacetamide, forms large, white crystals, melts at 68 — 69° , boils at 152 — 153° under 21 mm. pressure, is readily soluble in alcohol or ether, and sparingly so in water or light petroleum; it is not readily hydrolysed even by concentrated alkali hydroxides. The *sodium* derivative was prepared and analysed. When the nitrile is treated with silver nitrate, decomposition occurs with formation of a white, amorphous substance melting at 147 — 148° .

Phenylmethylcyanoacetiminoethyl ether, obtained by the action of methyl iodide on phenylmalononitrile in presence of sodium ethoxide, is an oily substance which has a slight aromatic odour, boils at 152 — 153° under 16 mm. and at 158 — 159° under 22—23 mm. pressure, has a sp. gr. 1.06 at 23° , is readily soluble in alcohol or ether, but insoluble in water; when its alcoholic solution is treated with strong hydrochloric acid, ammonium chloride is precipitated.

Phenylbenzylmalononitrile, prepared by the action of benzyl chloride and sodium ethoxide on phenylmalononitrile, crystallises in groups of needles, melts at 97 — 98° , is easily soluble in ether or alcohol, and is not affected by aqueous alkali hydroxides at 100° . E. G.

[Benzylmalimides.] O. Lutz (*J. pr. Chem.*, 1904, [ii], 70, 1—18. Compare Giustiniani, Abstr., 1892, 820; Ladenburg and Herz, Abstr., 1897, i, 460).—The two optically-active and the racemic benzylmalimides are formed when the corresponding benzylmalamic acids are heated at 150° in a vacuum.

r-Benzylmalimide forms colourless, monoclinic crystals, melts at 118° , and, with benzoic chloride, yields *i*-benzoylbenzylmalimide, which crystallises in small, white needles, melts at 100 — 101° , and is identical with Giustiniani's benzoyl derivative, which melted at 100° .

d-Benzylmalimide crystallises in rhombic, prismatic needles, melts at 105° , has $[\alpha]_D + 58.67^{\circ}$ at 18° , yields *d*-benzylmalamic acid on hydrolysis, and is identical with Giustiniani's β -imide. The *l*-imide has similar properties.

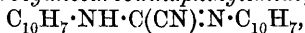
d-Benzoylbenzylmalimide melts at 126 — 127° , and has $[\alpha]_D + 24.7^{\circ}$. The *l*-compound melts at 126 — 127° and has $[\alpha]_D - 24.5^{\circ}$.

l-Benzylmalimide cannot be obtained in a state of purity by heating benzylamine hydrogen malate or a mixture of benzylamine and malic acid. In each case, the product consists of a mixture of the

active and racemic substances which cannot be completely separated. Giustiniani's α -imide and Ladenburg and Herz's β -imide (m. p. 102°) were similar mixtures. G. Y.

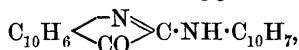
Condensation of Imines with α -Ethylenic Ketones. CHARLES MAYER (*Bull. Soc. chim.*, 1904, [iii], 31, 985—987. Compare this vol., i, 784).—When benzylideneaniline, dissolved in alcohol, is mixed with benzylideneacetone, dissolved in the same solvent, there separates after several days triphenylpiperidone, $\text{NPh} \begin{smallmatrix} \text{CHPh} \cdot \text{CH}_2 \\ \text{CHPh} \cdot \text{CH}_2 \end{smallmatrix} \text{CO}$, identical with that obtained by the condensation of acetone with benzylideneaniline (*loc. cit.*). This would seem to indicate that in the latter reaction the acetone first condenses with one molecule of benzylideneaniline to form the ketone, $\text{CHPh}(\text{NHPh}) \cdot \text{CH}_2 \text{Ac}$, which, by the loss of one mol. of aniline, forms benzylideneacetone, which, then reacts with a second mol. of the imine, forming triphenylpiperidone. This view, however, implies that the anilinophenylbutanone first formed is unstable, which is not the case with the analogous compounds described by Francis (*Trans.*, 1899, 75, 865; and 1902, 81, 441). T. A. H.

α -Naphthisatin- α -naphthalide and β -Naphthisatin- β -Naphthalide. CAMILLE DREYFUS and HENRY DREYFUS (D.R.-P. 152019).—Basic lead carbonate and potassium cyanide convert di- α -naphthylthiocarbamide into α -hydrocyanocarbodinaphthylimide,



which separates from benzene in yellow crystals and melts at 150°. β -Hydrocyanocarbodinaphthylimide is prepared in similar manner from di- β -naphthylthiocarbamide and melts at 166°. Concentrated sulphuric acid converts the imides into α -derivatives of naphthisatin, the β -compound being converted at the ordinary temperature, the α -compound preferably at 60°. When too strongly heated, insoluble products are obtained.

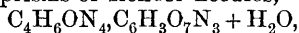
α -Naphthisatin- α -naphthalide, $\text{C}_{10}\text{H}_6 \begin{smallmatrix} \text{NH} \\ \text{CO} \end{smallmatrix} \text{C} : \text{N} \cdot \text{C}_{10}\text{H}_7$ or



forms a violet or reddish-brown precipitate. β -Naphthisatin- β -naphthalide dissolves in alcohol or benzene to reddish-brown solutions and melts above 180°. Heating with mineral acids removes naphthylamine, forming α - and β -naphthisatins (Hinsberg, *Abstr.*, 1888, 372).

C. H. D.

Correction [Imino-oxymethyltriazine]. ADRIANO OSTROGOVICH (*Gazzetta*, 1904, 34, ii, 75—77).—The data previously given by the author for imino-oxymethyltriazine picrate (*Abstr.*, 1897, i, 301) are to be corrected as follows. The picrate is formed by the action of picric acid on the base or its hydrochloride, best in presence of oxalic acid, which increases the solubility of the base in picric acid. It forms golden-yellow prisms or slender needles,



melting at 121—121.5°; the anhydrous salt melts at 224—224.5°.

T. H. P.

Condensations with Amino-acids. I. THEODOR CURTIUS (*J. pr. Chem.*, 1904, [ii], 70, 57—72. Compare *Abstr.*, 1902, i, 844).—An historical and theoretical introduction to the following papers.

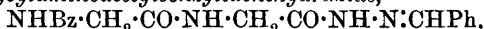
G. Y.

Condensations with Amino-acids. II. Formation of Glycyl Compounds by means of Hippurazoimide. THEODOR CURTIUS and RICHARD WÜSTENFELD (*J. pr. Chem.*, 1904, [ii], 70, 73—88. Compare foregoing abstract and *Abstr.*, 1902, i, 844).—By condensing hippurazoimide with glycine, esterifying the resulting acid, converting the ester into the hydrazide and azoimide, and repeating the foregoing operations on the latter product and another molecule of glycine, a series of acids varying from benzoylaminoacetic acid to benzoylpentaglycylaminoacetic acid has been prepared.

These acids are colourless, crystalline substances, which are only slightly soluble in alcohol or cold water, dissolve in aqueous alkalis, and yield colourless, crystalline, stable silver salts. The esters, which are best formed either by the action of ethyl iodide on the dry silver salt or by treating the acid with dilute alcoholic hydrochloric acid, are colourless, crystalline substances. The hydrazides and azoimides are colourless, crystalline substances; with increase in molecular weight, the former become less soluble in water, whilst the latter dissolve less readily in ether.

The following new substances are described.

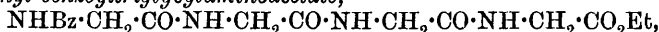
Benzoylglycylaminoacetylbenzylidenehydrazide,



crystallises in colourless leaflets and melts at 215—217°. *Benzoylglycylaminoacetanilide*, $\text{NHBz} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHPh}$, melts at 238—240°.

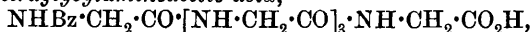
The *urethane*, $\text{NHBz} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO}_2\text{Et}$, corresponding with hippenylurethane (*Abstr.*, 1896, i, 38), is formed by the action of boiling alcohol on benzoylglycylaminoacetylazoimide. It crystallises in colourless leaflets, melts at 200°, and is hydrolysed by dilute sulphuric acid to benzoic acid, glycine, ammonia, formaldehyde, carbon dioxide, and alcohol.

Ethyl benzoyltriglycylaminoacetate,



crystallises in colourless leaflets and melts at 213°. The *hydrazide* crystallises in small, colourless leaflets and melts at 268°; the *azoimide* melts indefinitely at 245—258°.

Benzoyltetraglycylaminoacetic acid,



forms small, colourless leaflets and melts and decomposes at 246—252°.

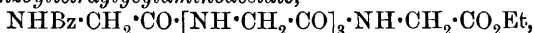
Benzoylpentaglycylaminoacetic acid crystallises in leaflets and melts and decomposes at about 268°. The melting point was found to be 280—285° by Curtius and Benrath (*this vol.*, i, 499). G. Y.

Condensations with Amino-acids. III. Formation of Glycyl Compounds by means of Hippurazoimide. THEODOR CURTIUS and LEO LEVY (*J. pr. Chem.*, 1904, [ii], 70, 89—108. Compare foregoing abstract).—Ethyl benzoyldiglycylaminoacetate is formed by the

action of hippurylazoimide on ethyl glycyllaminoacetate. *Benzoyldi-glycyllaminoacetylbenzylidenehydrazide* crystallises in small leaflets and melts at 264—265°. Benzoyldiglycyllaminoacetylazoimide is found to melt at about 236° and not at 162° as previously stated (Abstr., 1902, i, 844).

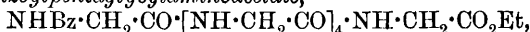
Benzoyltetraglycyllaminoacetic acid is formed by the action of benzoyldiglycyllaminoacetylazoimide on glycyglycine hydrochloride. When dried over sulphuric acid in a vacuum, the acid loses one mol. of water and yields a yellow, horny mass, $C_{17}H_{21}O_7N_5 \cdot H_2O$, which gives a violet coloration with Fehling's solution, melts and decomposes at 242—243°, and yields the acid when boiled with water.

Ethyl benzoyltetraglycyllaminoacetate,



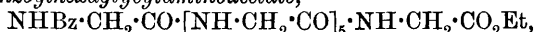
is formed by the action of ethyl iodide on the dry silver salt, or of benzoyldiglycyllaminoacetylazoimide on ethyl glycyllaminoacetate, or of benzoyltriglycyllaminoacetylazoimide on ethyl aminoacetate; it melts at 244—246°. The *hydrazide* melts and decomposes at 268—269°, and its *hydrochloride*, $NHBz \cdot CH_2 \cdot CO \cdot [NH \cdot CH_2 \cdot CO]_3 \cdot NH \cdot CH_2 \cdot CO \cdot N_2H_5 \cdot HCl$, melts at about 252°. An azoimide of this acid has not been obtained.

Ethyl benzoylpentaglycyllaminoacetate,



is formed by the action of ethyl iodide on the silver salt, or of benzoyltriglycyllaminoacetylazoimide on ethyl glycyllaminoacetate, or of hippurylaminoacetylazoimide on ethyl triglycyllaminoacetate (Curtius, this vol., i, 477). It melts at 258—263°.

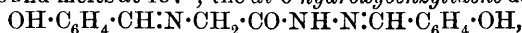
Ethyl benzoylhexaglycyllaminoacetate,



formed from benzoyldiglycyllaminoacetylazoimide and ethyl triglycyllaminoacetate, is red and melts at 274—277°.

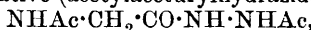
Aminoacetylhydrazide, $NH_2 \cdot CH_2 \cdot CO \cdot NH \cdot NH_2$, is formed by the action of hydrazine hydrate on ethyl aminoacetate. It solidifies to a transparent, stellate mass, melts at 80—85°, and decomposes at 150°. It is moderately soluble in chloroform, less so in absolute alcohol, almost insoluble in ether or light petroleum; when exposed to air, it deliquesces and absorbs carbon dioxide. With mercuric chloride in aqueous solution, it gives a white, granular precipitate; it reduces Fehling's solution and gives a marked biuret reaction. The *hydrochloride*, $C_2H_5ON_3 \cdot 2HCl$, melts at 200—201°.

The *benzylidene* derivative, $NH_2 \cdot CH_2 \cdot CO \cdot NH \cdot N : CHPh$, crystallises in thin leaflets and melts at 157°; the *di-o-hydroxybenzylidene* derivative,

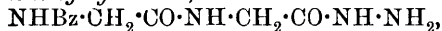


crystallises in yellow leaflets and melts at 189—191°; the *di-β-propylidene* derivative, $CMe_2 \cdot N \cdot CH_2 \cdot CO \cdot NH \cdot N : CMe_2$, crystallises in long needles, melts at about 79°, and decomposes at 215°; the *compound* with ethyl acetoacetate, $NH_2 \cdot CH_2 \cdot CO \cdot NH \cdot N : CMe \cdot CH_2 \cdot CO_2Et$, commences to decompose at 280° and melts at 290°.

The *diacetyl* derivative (acetylaceturylhydrazide),



crystallises in microscopic needles and melts at 183.5°; the *dibenzoyl* derivative (benzoylhippurylhydrazide), $NHBz \cdot CH_2 \cdot CO \cdot NH \cdot NHBz$, crystallises in small needles and melts at 213°.

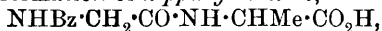
Hippurylaminoacetylhydrazide,

formed by the action of hippurylazoimide on aminoacetylhydrazide, crystallises in small leaflets and melts at 230° .

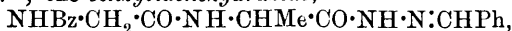
The action of iodine on aminoacetylhydrazide in concentrated aqueous solution leads to the formation of a colourless substance which is probably the dihydrazide of glycine.

The action of sodium nitrite and hydrochloric acid on aminoacetylhydrazide in aqueous solution, under ether, leads to the formation of an ethereal solution which, with aniline, yields a substance melting at 185° . The diazotised aqueous solution after some time developed an odour of hydrazoic acid, which, on boiling, was followed by that of formaldehyde. G. Y.

Condensations with Amino-acids. IV. Action of Hippurylazoimide on α -Alanine. THEODOR CURTIUS and EMIL LAMBOTTE (*J. pr. Chem.*, 1904, [ii], 70, 109—128. Compare foregoing abstracts).—The action of hippurylazoimide on alanine in aqueous solution leads to the formation of *hippurylalanine*,



which crystallises in colourless needles and melts at 202° . It is soluble in water or alcohol, almost insoluble in ether, benzene, or chloroform; the aqueous solution reddens litmus. The *ammonium* salt crystallises in white needles; the *silver* salt crystallises in small colourless leaflets; the *copper* salt forms blue needles. The *ethyl* ester, formed by the action of ethyl iodide on the silver salt, or of dilute alcoholic hydrochloric acid on the acid, crystallises in small, colourless needles and melts at 124 — 126° ; the *methyl* ester crystallises in small needles and melts at 136° ; the *amyl* ester forms colourless leaflets and melts at 96° . The *hydrazide* crystallises in long, thin needles and melts at 187° ; the *benzylidenehydrazide*,



melts at 216° ; the *azoimide* forms microscopic crystals, melts and decomposes at 101 — 102° , and, when boiled with alcohol, yields the *urethane*, $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, which crystallises from alcohol, melts at 205° , and is hydrolysed by cold dilute sulphuric acid. The *amide*, $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}_2$, melts at 195° and evolves ammonia when treated with alkalis. The action of aniline on the azoimide in alcoholic solution leads to the formation of the *phenylcarbamide* derivative,



which forms a flocculent precipitate and melts at 216° . Its behaviour to dilute sulphuric acid is analogous to that of the urethane.

Hippuryl- α -alanyl- α -alanine,

formed by the action of hippurylalanylazoimide on alanine at -5° to -10° , forms small, colourless needles and melts at 120 — 130° ; the *silver* salt forms leaflets which become brown on exposure to light; the *ethyl* ester melts at 174 — 175° ; the *methyl* ester crystallises in small needles and melts at 180 — 181° ; the *amyl* ester forms small leaflets and melts at 155° ; the *hydrazide* melts at 213° ; the *benzylidene*-

hydrazide melts at 238°; the *azoimide* melts and decomposes at about 145°. The action of ethyl alcohol on the *azoimide* leads to the formation of the *urethane*,

$\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, which crystallises in colourless leaflets and melts at 203°; the action of ammonia on the *azoimide* leads to the formation of the *carbamide*, $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, which melts at 199°; that of aniline gives rise to the *phenylcarbamide* derivative, which melts at 226°.

Hippuryldi- α -alanyl- α -alanine,

$\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, formed from hippuryldialanylazoidimide and alanine, crystallises in colourless, delicate needles and melts at 230°. G. Y.

Is α -Thiolactic Acid a Direct Decomposition Product of Proteids? KARL A. H. MÖRNER (*Zeit. physiol. Chem.*, 1904, 42, 365—370. Compare Suter, Abstr., 1895, i, 691; Friedmann, 1903, i, 75, 301).—The proteid was heated with 2—4 parts of 15 per cent. hydrochloric acid for several days at 90° in a closed flask. A 6 per cent. yield of cystin was obtained, but neither α -thiolactic acid nor its disulphide could be detected in the aqueous extracts. Minute traces of the α -thio-acid appear to be formed when the heating is prolonged and when sulphur and hydrogen sulphide begin to be formed; it is, therefore, not a primary but a secondary product of decomposition. Friedmann's acid was either formed by the action of hydrogen sulphide on pyruvic acid or by the decomposition of cystin.

The whole of the sulphur which can be eliminated by warming with sodium hydroxide is thought to be combined in the proteid molecule in the form of a cystin group. J. J. S.

Decomposition Products of Cystin. KARL A. H. MÖRNER (*Zeit. physiol. Chem.*, 1904, 42, 349—364. Compare Friedmann, Abstr., 1902, i, 731; Neuberg, *ibid.*, 743).—Both α - and β -thiolactic acids (Loven, Abstr., 1884, 1298), give the reddish-purple coloration with ferric chloride which is usually described as characteristic of thioglycollic acid. The permanent violet coloration which the α -acid gives with copper sulphate solution is best obtained by using a dilute solution of the acid and an excess of the copper sulphate, otherwise a yellowish-grey precipitate may be formed.

Suter's benzyl- α -thiolactic acid (Abstr., 1895, i, 691) melts at 76.5 and not at 74°. Benzyl- β -thiolactic acid crystallises in rhombic plates, melts at 81—81.5°, and is more readily soluble in water than the α -compound.

α -Thiolactic acid is obtained when cystin is reduced to cystein, and the hydrochloride of this is heated in aqueous solution at 140—150° and extracted with ether. β -Thiolactic acid and thioglycollic acid do not appear to be formed under these conditions, and in only one case has pyruvic acid been detected.

Among the other products obtained were hydrogen sulphide, ammonia (some 50 per cent. of the total nitrogen in cystin), and alanine.

It is probable that both β -amino- α -thiolactic acid and α -amino- β -

thiolactic acid are present in the cystin used. The former, on hydrolysis, would yield ammonia and α -thiolactic acid, the latter, hydrogen sulphide and alanine.
J. J. S.

Philothion. J. DE REY PAILHADE (*Bull. Soc. chim.*, 1904, [iii], 31, 987—991. Compare Abelous and Ribaut, this vol., i, 704).—Products of the activity of living cells capable of hydrogenating sulphur at temperatures not exceeding 45° should alone be regarded as containing philothion.

The results of a number of experiments with egg-albumin coagulated under various conditions showed that the activity of the philothion is not inhibited when the albumin is coagulated alone or in presence of dilute acids, but its activity is destroyed by coagulation in presence of dilute alkalis or by the action of these substances on active coagulated albumin. The philothion of raw egg-albumin is much more susceptible to the action of acids than is that of coagulated albumin.

The discontinuous curves obtained by Abelous and Ribaut representing the influence of temperature on the rate of production of hydrogen sulphide by animal extracts (*loc. cit.*) each consists of two portions, one due to "physiological" philothion and the other to philothion condensed by coagulation.

This action of certain proteids on sulphur furnishes a method of distinguishing between serum-albumin, which is inactive, and other intracellular albumins and egg-albumin (compare Heffter and Hausmann, this vol., i, 461), and may be used for the detection of albumins of the latter class in urine, &c. Experiments in this direction with an extract from the kidney of a horse gave positive results, whereas the urines of several persons suffering from albuminuria gave negative results.
T. A. H.

Thymus Nucleic Acid. I. HERMANN STEUDEL (*Zeit. physiol. Chem.*, 1904, 42, 165—170).—Neumann's α -nucleic acid (*Abstr.*, 1900, i, 319) has been hydrolysed by boiling with hydriodic acid in the presence of phosphorous acid and the amounts of nitrogenous products determined. If the original amount of nitrogen is represented by 100, then 11.54 per cent. is found in the form of humus; 7.00 as ammonia; 3.61 as guanine; 13.45 as adenine; 6.74 as xanthine; 5.20 as hypoxanthine; 11.45 as cytosine, and 15.88 as thymine and uracil, the total nitrogen accounted for being about 75 per cent.
J. J. S.

Presence in Nucleic Acids of a Radicle which yields Lævulic Acid. KATSUJI INOUE (*Zeit. physiol. Chem.*, 1904, 42, 117—120. Compare Kossel and Neumann, *Abstr.*, 1894, ii, 631; Noll, 1898, i, 718; and Araki, 1903, i, 668).—Lævulic acid has been obtained from the products of hydrolysis of spleen nucleic acid (compare Levene, *Zeit. physiol.*, 1902, 37, 402), of the nucleic acid from the testicles of oxen (Levene, this vol., i, 126), and of the nucleic acid from the spermatozoa of *Muraenox cinereus*.
J. J. S.

Pure Glycogen. Z. GATIN-GRUZEWSKA (*Pflüger's Archiv*, 1904, 102, 569—591).—Glycogen has been prepared by the Pflüger-Nerking method (Abstr., 1899, ii, 819), freed from small amounts of nitrogen derivatives by treatment with 30 per cent. potassium hydroxide on the water-bath, then diluted with water and precipitated with 97 per cent. alcohol. The precipitation with alcohol after solution in water is repeated some five or six times in order to remove all the alkali. Inorganic impurities are removed by the addition of a little acetic acid to the solution, as recommended by Bernard (*Compt. rend.*, 1857, 44, 578). After repeated precipitation with alcohol (16—18 times), the solid glycogen is washed for two days with absolute alcohol, and then with ether which is free from acid. It is desiccated over calcium chloride or phosphoric oxide, and may be dried at 100° without losing colour, but in that case should be previously heated at 60° for a day.

When dried in a vacuum desiccator over sulphuric acid, it appears to be acted on by sulphur dioxide, and is then not completely soluble in water and has a lower rotatory power. The specimens obtained were nearly all free from ash and from nitrogen. The analyses agree with the formula $C_6H_{10}O_5$, and freshly prepared specimens give $[\alpha]_D$ 196.6 (mean of four determinations). In estimating glycogen by hydrolysis with hydrochloric acid and weighing the cuprous oxide obtained with Fehling's solution, the numbers obtained should be multiplied by 0.927 (compare Nerking, Abstr., 1901, ii, 462).

The solubility of glycogen in aqueous alcohol varies considerably with the temperature, and the amount of alcohol required for precipitation diminishes with the concentration of the solution.

Clear solutions of glycogen, when placed for some time in a burette, become more concentrated in the lower part and less concentrated in the upper. Under certain conditions, the precipitated glycogen has a characteristic appearance under the microscope, and occasionally crystals of the pure compound have been obtained. Only the pure compound gives these characteristic forms, and when pure it does not adhere to glass in the same manner as a slightly impure glycogen.

J. J. S.

Guanase. WALTER JONES and C. L. PARTRIDGE (*Zeit. physiol. Chem.*, 1904, 42, 343—348).—The fact that nucleoproteids, when allowed to undergo autolysis, yield products different from those obtained by the hydrolysis of the same nucleoproteids with acids, is accounted for by the presence of an enzyme, or enzymes, which, during the autolysis, decomposes guanine into xanthine, and adenine into hypoxanthine and ultimately into xanthine. Fresh pancreas, when subjected to autolysis, does not yield adenine or guanine, and guanine which is added is transformed into xanthine within 3 days. The enzyme present in pancreas which induces this change is termed *Guanase*. A similar, or identical, enzyme exists in thymus and kidneys, but not in the spleen. Spleen contains an enzyme *adenase*, which transforms adenine into hypoxanthine in the absence of *guanase*. When thymus nucleoproteid is precipitated, washed with alcohol and

ether, and kept in a desiccator for 2 weeks, and then allowed to undergo autolysis, the products are adenine and guanine. J. J. S.

Colouring Matter of Blood. Formula for Hæmin. II. J. HETPER and LEON MARCHLEWSKI (*Zeit. physiol. Chem.*, 1904, 42, 65—69. Compare this vol., i, 463; Küster, *ibid.*, 357).—Hæmin has been prepared by using propionic in place of the usual acetic acid; the product is identical with the so-called acethæmin in all physical and optical properties, and the conclusion is drawn that no acetyl groups, whether attached to O, N, or C, can be present in the hæmin ("acethæmin") molecule. The formula $C_{34}H_{33}O_4N_4ClFe$ is confirmed. J. J. S.

Melanotic Pigments. HANS WOLFF (*Beitr. chem. Physiol. Path.*, 1904, 5, 476—488).—In a melanotic liver, two pigments were separated by the use of sodium hydroxide, one being soluble, the other insoluble in this reagent. The soluble pigment has a lower percentage of carbon than most melanins, and contains iron; the other contains no iron and only traces of sulphur. From another strongly melanotic liver, a pigment was separated the individuality of which was attested by analyses. It contains at least 15 per cent. of a hydro-aromatic substance which is shown to be identical with xylitone; isovaleronitrile was also prepared from it in amount corresponding with 2.5 per cent. of the melanin; a third product which was isolated could not be identified. No sulphur-yielding substance was obtained by oxidation, so nothing can be said of the way the sulphur is combined. The pigment contains 1.7 per cent. of sulphur.

W. D. H.

Action of Heat and Acidity on Dissolved Amylase. PAUL PETIT (*Compt. rend.*, 1904, 138, 1716—1718. Compare this vol., i, 541).—An aqueous infusion of malt, on being heated at 100°, coagulates, thickens without coagulation, or remains limpid, according to the amount of free acid present in the original solution. Representing the acidity which promotes coagulation by unity, the other two values are represented by 2 and 3 respectively when hydrochloric acid is the acid added, or 3 and 6 respectively when lactic acid is added. The action of heat on the infusions is to cause an increase in the acidity up to the point where coagulation begins. The diastatic power of malt infusions varies with the acidity, reaching a maximum for that quantity of acid which determines the beginning of coagulation. M. A. W.

Action of Maltase. Stability of the Ferment. Influence of the Products of the Reaction. Mlle. CH. PRILACHE (*Compt. rend.*, 1904, 138, 1634—1636. Compare this vol., ii, 318).—The velocity of hydrolysis by maltase (taka-diastase) of solutions containing varying proportions of maltose and dextrose was measured polarimetrically and it was found that the ferment retains its initial activity during a period of 38 hours in the presence of the products of the reaction. The presence of dextrose retards the hydrolysis, thus the rotatory power, after 30 hours, of a solution initially containing 4 per cent. of

maltose was 4.12° , and the addition of 10 or 20 per cent. of dextrose to a similar solution lowered the rotatory power to 2.92° and 2.77° respectively.

M. A. W.

Existence in Plants of an Oxidising-reducing Diastase. Conditions of its Action. J. E. ABELOUS (*Compt. rend.*, 1904, 138, 1619—1620. Compare Abstr., 1903, ii, 560; this vol., ii, 188, 283).—The oxidising-reducing diastase present in the potato converts salicylaldehyde into salicylic acid under conditions in which the normal diastases are inoperative, namely, in the absence of air, and when the vegetable cells are not destroyed by pressure.

M. A. W.

Formation of Carbamide by Fermentations. ALBRECHT KOSSEL and HENRY D. DAKIN (*Zeit. physiol. Chem.*, 1904, 42, 181—188. Compare this vol., ii, 425).—The reactions of arginase with precipitating agents and solvents are not exactly the same as those of lipo- α - or - β -protase (Hedin, *Jour. Physiol.*, 30, 155). Liver has the greatest power of decomposing arginine; nerves, thymus, and lymph glands are also active, but blood and muscles have practically no action.

The proton (*loc. cit.*) obtained from clupein is termed β -clupeon. It differs from Kossel and Goto's α -clupeon in yielding only 69.7 per cent. of its total nitrogen as arginine instead of 80. On hydrolysis with dilute sulphuric acid, β -clupeon yields ornithine, whereas clupein does not.

J. J. S.

Animal Lactase. H. BIERRY and G. SALAZAR (*Compt. rend.*, 1904, 139, 381—384).—The juices from the pancreas and the intestine do not contain any of the lactose-splitting enzyme. The fluid obtained by maceration of intestinal mucus only shows the presence of lactase if cellular elements are present, or if the fluid has been in contact with these *in vitro* for a sufficiently long time. In the case of the dog, lactase has been found in the small intestine, but not in the stomach or the large intestine; it is also present in the fœtus of the cow or ewe. The activity of animal lactase is favoured by slight acidity (0.02—0.04 gram of hydrochloric or acetic acid per litre). A larger quantity (0.5—1 gram per litre) stops the action completely. Alkalis have a retarding effect when present to the extent of a few centigrams per litre.

H. M. D.

Organic Chemistry.

Addition of Bromine to Carbon Atoms united by a Double Linking. HUGO BAUER (*Ber.*, 1904, 37, 3317—3321).—Observations made by other investigators on the addition of bromine in diffused daylight are brought together and the following generalisations drawn. In the system $\text{CO}_2\text{H}\cdot\text{CH}\cdot\text{CH}_2$, bromine is added so long as all three hydrogen atoms are not replaced by bromine or by bromine and methyl. With three methyl groups, for example, trimethylacrylic acid, the power of uniting with bromine is still retained (W. H. Perkin, jun., *Trans.*, 1896, 69, 1480).

With two carboxyl groups, for example, $\text{CO}_2\text{H}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, addition is possible so long as both hydrogen atoms are not replaced by bromine or methyl, for example, dimethylfumaric, dibromofumaric, and bromomesaconic acids do not form dibromides. Ethylene-tetracarboxylic acid and tetraphenylethylene do not unite with bromine.

In styrene, $\text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{CH}_2$, addition of bromine is possible when all three hydrogens are replaced by methyl. With stilbene, $\text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_5$, addition is no longer possible when the two hydrogens are replaced by bromine. With $\text{CPh}_2\cdot\text{CH}_2$, the replacement of one hydrogen by bromine is sufficient to prevent the addition of bromine, but if one or both hydrogens are replaced by methyl, addition can still take place.

J. J. S.

$\alpha\epsilon$ -Dibromopentane. JULIUS VON BRAUN (*Ber.*, 1904, 37, 3210—3213).— $\alpha\epsilon$ -Dibromopentane is conveniently prepared in quantity by heating benzoylpiperidine with phosphorus pentabromide and fractionating the resulting mixture under reduced pressure; it boils at $220\text{--}222^\circ$ or at $104\text{--}105^\circ$ under 14 mm. pressure and reacts with aniline to form 1-phenylpiperidine (compare Lellmann, *Abstr.*, 1887, 604) boiling at $257\text{--}258^\circ$.

E. F. A.

Decomposition of Di-iodoacetylene. RUDOLF SCHENCK and J. LITZENDORFF (*Ber.*, 1904, 37, 3453—3464. Compare Baeyer, *Abstr.*, 1885, 1199; Meyer and Pemsel, *ibid.*, 1896, i, 517).—The di-iodoacetylene used was prepared by Biltz's method (*Abstr.*, 1897, i, 389), and also from tetraiodoethylene by Nef's method (*Annalen*, 1897, 298, 341). When the di-iodoacetylene is heated in benzene solution at 100° , carbon is deposited; this, however, is not pure but contains iodine compounds and benzene, which are only removed by heating the carbon in a current of hydrogen at a relatively high temperature.

The equilibrium $\text{C}_2\text{I}_4 \rightleftharpoons \text{C}_2\text{I}_2 + \text{I}_2$ has been determined by heating a solution of tetraiodoethylene in benzene at 138° for different lengths of time. Equilibrium is attained after about 4 hours when 4 per cent. of the tetraiodo-compound is decomposed. When ethylene dibromide is used as solvent, equilibrium is reached when 8.8 per cent. is decom-

posed. Previous heating of the solution at 55° has no effect, whereas equilibrium is attained in a much shorter time in tubes previously exposed to sunlight.

The decomposition of di-iodoacetylene, $2\text{C}_2\text{I}_2 = \text{C}_2\text{I}_4 + \text{C}_2$, has been investigated in various solutions and at different temperatures by weighing the amount of carbon deposited. In all cases, before weighing, the carbon was heated in a stream of hydrogen. The results indicate that the reaction is unimolecular, and constants have been obtained by aid of the equation $K = 1/t \log a/a - x$. The influence of temperature is shown by the following numbers obtained for benzene solutions: 100°, $K = 0.0002$; 110°, $K = 0.00047$; 138°, $K = 0.0071$. The influence of the solvent is not so marked, the smallest numbers were obtained with toluene solutions.

The reaction is considerably accelerated by the presence of catalysers, more especially of solid mercuric iodide. In the presence of this reagent, the constant tends to increase with the time, probably owing to the fact that more of the catalyser dissolves in the solvent (benzene) as the time proceeds.

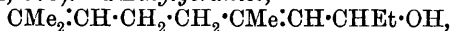
The nature of the glass does not appear to affect the rate of decomposition.

When benzene solutions of di-iodoacetylene are heated at 100°, it is found that the solutions can remain quite clear for several hours and then the deposition of carbon begins suddenly, and during the next half hour a considerable amount of decomposition occurs. It is probable that the finely divided carbon itself acts as a catalyser and that the decomposition takes place on the surface of this precipitated carbon.

Good photographic paper can be made by impregnating paper with a benzene solution of di-iodoacetylene. The great drawback is the obnoxious odour.

The decomposition of di-iodoacetylene by alcoholic potash (compare Nef, *loc. cit.*) is regarded as a reaction between nascent carbon and alkali and is thus comparable with the action of other non-metals, for example, chlorine, sulphur, and phosphorus, on alkalis. J. J. S.

α -Derivatives of Geraniol. FARBENFABRIKEN VORM FRIEDR. BAYER & Co. (D.R.-P. 153120).— α -Alkyl- or -aryl-geraniols may be prepared from citral and magnesium alkyl or aryl haloids, the resulting double compounds being decomposed by water or dilute acids. When strong acids are employed, hydrocarbons are produced (Grignard, *Abstr.*, 1901, i, 679). *α -Ethylgeraniol*,



boils at 120° under 14 mm. pressure. *α -Methylgeraniol* is a colourless liquid boiling at 112–113° under 12 mm. pressure. *α -Phenylgeraniol* is a slightly yellow, highly refracting oil, boiling at 175–176° under 12 mm. pressure. The rose-like odour of these oils is stronger than that of geraniol. C. H. D.

A Crystalline Compound of Lead Thiosulphate and Acetate, $2\text{PbS}_2\text{O}_3\cdot\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$. PAUL LEMOULT (*Compt. rend.*, 1904, 139, 422–424).—Lead thiosulphate, obtained by adding a solution of lead

acetate to one of sodium thiosulphate, dissolves in acetic acid, and from the solution a double salt having the composition $2\text{PbS}_2\text{O}_3 \cdot \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ separates in the form of hard, thin, white, needle-shaped crystals 3 to 4 mm. long, very slightly soluble in cold water, less so in dilute acetic acid, and more so in boiling water, from which it can be crystallised.

M. A. W.

Theory of Saponification. RICHARD FANTO (*Monatsh.*, 1904, 25, 919—928. Compare Geitel, *Abstr.*, 1897, ii, 547; Balbiano, this vol., i, 216).—The author has been unable to find a solvent which, whilst not entering into the reaction, will permit the hydrolysis of triglycerides to be carried out in a homogeneous solution. In several experiments on the partial hydrolysis of triglycerides, the glycerol obtained corresponded with the potassium hydroxide which was neutralised; neither di- nor mono-glycerides could be detected amongst the products, and if these are formed in the course of the reaction they must immediately undergo further hydrolysis. The saponification of triglycerides by potassium hydroxide is, at least seemingly, a quadrimolecular reaction.

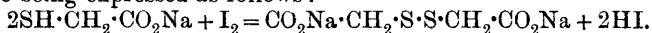
G. Y.

Synthesis of Stearic Acid by means of the Electric Discharge. ALEXANDRE DE HEMPTINNE (*Bull. Acad. Roy. Belg.*, 1904, 550—556).—Under the influence of the electric discharge, oleic acid is converted into stearic acid to the extent of about 50 per cent. in 10 hours. The apparatus used is described in detail. E. F. A.

Formation of Complex Salts with Thio-acids. Thio-glycollates. ARTHUR ROSENHEIM and ISSER DAVIDSOHN (*Zeit. anorg. Chem.*, 1904, 41, 231—248).—The majority of investigations with complex salts have hitherto been conducted with salts where the cation is complex. The authors have examined cases where the anion is complex and contains sulphur, with the view of determining whether thio-acids form complex compounds with such electronegative elements, which otherwise exhibit little tendency to the formation of complexes. The metallic derivatives of ethyl xanthate studied by Hasliwetz do not suffer normal dissociation.

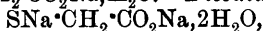
When an alcoholic solution of potassium xanthate is boiled with an excess of cobaltous chloride, dark green needles separate, which Hasliwetz supposes to be cobaltous xanthate; the compound is, however, a cobaltic salt, $(\text{OEt} \cdot \text{CS}_2)_3\text{Co}$. The nickel salt, prepared in an analogous manner, has the composition $(\text{OEt} \cdot \text{CS}_2)_2\text{Ni}$.

Solutions of thioglycollic acid or of its sodium and potassium salts are very readily oxidised. The analysis of the thio-glycollates described was accordingly conducted iodometrically, the reaction of the salts dissolved in a solution of sodium hydrogen carbonate and acted on by iodine being expressed as follows:



Monosodium thioglycollate, $\text{SH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Na} \cdot 3\text{H}_2\text{O}$, prepared from sodium hydrosulphide and monochloroacetic acid, separates in needles

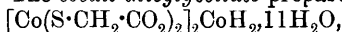
and has a neutral reaction. When dried over sulphuric acid, it forms its *monohydrate*, $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}\cdot\text{H}_2\text{O}$. *Disodium thioglycollate*,



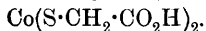
separates in prisms and has an alkaline reaction. *Magnesium thioglycollate*, $\text{CH}_2\left\langle\begin{smallmatrix} \text{CO}_2 \\ -\text{S} \end{smallmatrix}\right\rangle\text{Mg}\cdot 8\text{H}_2\text{O}$, crystallises in prisms. *Manganese*

thioglycollate contains $7\text{H}_2\text{O}$ and separates in pink prisms. *Zincothioglycollic acid*, $\text{Zn}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2\cdot\text{H}_2\text{O}$, prepared by the action of zinc on thioglycollic acid, separates in needles. *Sodium zinc thioglycollate*, $\text{Na}_2\text{Zn}_2(\text{C}_2\text{H}_2\text{O}_2\text{S})_3\cdot 4\text{H}_2\text{O}$, forms needles. *Barium zinc thioglycollate*, $\text{BaZn}_2(\text{C}_2\text{H}_2\text{O}_2\text{S})_3\cdot 3\text{H}_2\text{O}$, is formed from the preceding salt by the addition of barium chloride. The two latter salts are derivatives of a complex zinc thioglycollic acid, the zinc being in the complex anion. For comparison, zinc alkali thiosulphates were prepared. *Potassium zinc thiosulphate*, $\text{K}_2\text{Zn}(\text{S}_2\text{O}_3)_2\cdot\text{H}_2\text{O}$, and *ammonium zinc thiosulphate*, $(\text{NH}_4)_2\text{Zn}(\text{S}_2\text{O}_3)_2\cdot\text{H}_2\text{O}$, separate from water in prisms; both salts are very soluble in water and give the reactions for the zinc ion, which the corresponding glycollates do not.

The double salt of cadmium thioglycollate and sodium chloride, $\text{Cd}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na})_2\cdot 3\text{NaCl}\cdot 6\text{H}_2\text{O}$, separates in prisms and may be crystallised from water without change. *Barium cadmiothioglycollate*, $\text{Cd}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2)_2\cdot\text{Ba}\cdot 18\text{H}_2\text{O}$, is crystalline. *Sodium nickelothioglycollate*, $\text{Ni}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na})_2\cdot 4\text{H}_2\text{O}$, forms green needles. In contradistinction to the zinc and cadmium salts described, the nickel in the complex is only feebly bound, since solutions of the salt readily give the reactions for the nickel ion. The *cobalt thioglycollate* prepared,



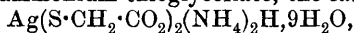
is the hydrogen cobaltous salt of cobaltothioglycollic acid,



Sodium cobaltothioglycollate, $\text{Co}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na})_2\cdot 6\text{H}_2\text{O}$, forms dark reddish-brown needles with a green lustre. *Barium cobaltothioglycollate*, $\text{Co}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2)_2\cdot\text{Ba}\cdot 12\text{H}_2\text{O}$, is dark brown. The three latter salts do not exhibit the reactions of the cobalt ion.

Ammonium cobaltothiosulphate, $(\text{NH}_4)_6\text{Co}_2(\text{S}_2\text{O}_3)_5\cdot 6\text{H}_2\text{O}$, forms greenish-blue prisms, solutions of which give the reactions for the cobalt ion.

Sodium lead thioglycollate, $[\text{Pb}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2)_2]_2\text{PbNa}_2\cdot 2\text{H}_2\text{O}$, forms yellow needles; addition of sodium hydroxide to its solution causes no precipitate. *Sodium copper thioglycollate*, $\text{Na}_3\text{Cu}_5(\text{C}_2\text{H}_2\text{O}_2\text{S})_4\cdot\text{H}_2\text{O}$, separates in greenish-white needles. *Sodium silver thioglycollate*, $\text{Na}_4\text{Ag}_2(\text{C}_2\text{H}_2\text{O}_2\text{S})_3$, has an alkaline reaction; when potassium hydroxide is added to its solution, no precipitate is formed. When silver chloride is dissolved in ammonium thioglycollate, iridescent needles of *ammonium silver glycollate*, $\text{SAg}\cdot\text{CH}_2\cdot\text{CO}_2\text{NH}_4$, separate. When dissolved in ammonium thioglycollate, the salt,



separates in needles.

Bismuth thioglycollate, $\text{Bi}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_3$, separates in dark yellow crystals. *Bismuth bismuthothioglycollate*, $\text{Bi}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2)_3\text{Bi}$, is a dark yellow, crystalline powder. The salt,



crystallises in yellow needles. The addition of water to these bismuth salts causes no precipitate of basic salts and the addition of ammonia no precipitate of hydroxide, but their alkaline solutions undergo gradual decomposition.

Potassium bismuthothioglycollate, $\text{Bi}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{K})_3\cdot 6\text{H}_2\text{O}$, crystallises in yellow prisms. The salt, $\text{OH}\cdot\text{Bi}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na})_2\cdot 10\text{H}_2\text{O}$, forms yellow needles.

Antimoniothioglycollic acid, $\text{Sb}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_3\cdot 12\text{H}_2\text{O}$, crystallises in transparent pyramids.

Arseniothioglycollic acid, $\text{As}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_3\cdot \frac{1}{2}\text{H}_2\text{O}$, forms transparent tetrahedra.

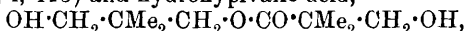
The "Komplexzerfallkonstante" of several of the thioglycollates described were determined by von Euler (compare Abstr., 1903, ii, 544, 717; this vol., ii, 11, 379). Those values for sodium cadmium thioglycollate and sodium lead thioglycollate respectively are at least 10^6 times as small as the values for the corresponding thiosulphates.

A. McK.

Antimony Double Lactates. B. MORITZ (*Zeit. angew. Chem.*, 1904, 17, 1143—1148).—Polemical. A reply to Jordis (Abstr., 1902, i, 740; this vol., i, 468).

A. McK.

Condensations by means of Magnesium Ethyl Iodide. ADOLF FRANKE and MORITZ KOHN (*Monatsh.*, 1904, 25, 865—870. Compare Kling, this vol., i, 2).—The action of magnesium ethyl iodide on the aldol from formaldehyde and isobutaldehyde (Wessely, Abstr., 1900, i, 428) leads to the formation of an ester of Just's pentaglycol (Abstr., 1896, i, 413) and hydroxyypivalic acid,



which separates from light petroleum in stellate aggregates of crystals, melts at 51° , and boils at 156° under 10 mm. pressure. When hydrolysed with aqueous potassium hydroxide, the ester yields pentaglycol and hydroxyypivalic acid.

Along with the ester there are formed trioxymethylene, the last traces of which can be separated from the ester only by prolonged boiling in a reflux apparatus, and a viscid, colourless oil, which boils at 110° under 10 mm. and at 200 — 220° under atmospheric pressure.

G. Y.

Acetylation of Ethyl Cyanoacetate. WALTER DIECKMANN and FRITZ BREEST (*Ber.*, 1904, 37, 3384—3387).—Ethyl cyanoacetate yields ethyl cyanoacetoacetate when boiled with acetic anhydride and sodium acetate, and when treated with acetic anhydride and pyridine or with acetyl chloride and pyridine in the cold (compare Claisen and Haase, Abstr., 1900, i, 373). The best yield, 60 per cent. of the theoretical, is obtained by the interaction of ethyl cyanoacetate (1 mol.), pyridine (2 mols.), and acetic chloride ($1\frac{1}{2}$ mols.). The product is isolated as the green copper compound, $(\text{C}_7\text{H}_8\text{O}_3\text{N})_2\text{Cu}$, which crystallises from a mixture of alcohol and chloroform and melts at 235° . On prolonged boiling with acetic anhydride and pyridine, ethyl cyanoacetate yields cyanoacetylacetone.

Ethyl cyanoacetate does not form ethyl cyanoacetoacetate when boiled with acetic anhydride and quinoline or dimethylaniline.

G. Y.

Constitution of Ethyl Acetoacetate. LUDWIG KNORR (*Ber.*, 1904, 37, 3488—3489. Compare Abstr., 1899, i, 673).—In the light of the results obtained by Knorr and Hörlein (see succeeding abstract), the non-occurrence of the ammonia reaction with ethyl acetoacetate is no proof of the absence of the enolic modification, and the author's former conclusion, that the enolic and ketonic modifications exist together in a state of equilibrium, is probably correct.

C. H. D.

The Application of Hantzsch's Ammonia Reaction to the Enolic Forms of Ethyl Diacetylsuccinate. LUDWIG KNORR and H. HÖRLEIN (*Ber.*, 1904, 37, 3490—3493).—The seven known modifications of ethyl diacetylsuccinate, five of which are enolic, yield no precipitate with ammonia in ethereal solution. A solution of the β -ester in ether, which had been heated at 120°, gave an amorphous precipitate of ammonium ethyl isocarbopyrotritarate with ammonia. Ethyl isocarbopyrotritarate is known to be formed on heating ethyl diacetylsuccinate. The statement of Hantzsch and Dollfus (*Abstr.*, 1902, i, 233, 675) that the enolic modifications of ethyl diacetylsuccinate yield precipitates with ammonia in ethereal solution is erroneous, and is due to the presence of acid impurities in the ester employed by them. Hantzsch's ammonia reaction is, therefore, not a trustworthy method of distinguishing ketonic from enolic compounds, but may be used to distinguish strongly enolic compounds, such as the hydroxy-methylene derivatives, from weak enols.

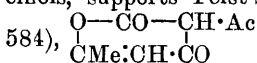
C. H. D.

Constitution of Dehydracetic Acid. WALTER DIECKMANN and FRITZ BREEST (*Ber.*, 1904, 37, 3387—3392).—When boiled with acetic anhydride in presence of a trace of acetic chloride, triacetic- δ -lactone forms an *anhydride*, $O \begin{smallmatrix} \diagup \text{CO} \text{---} \text{CH} \\ \diagdown \text{CMe} \text{:} \text{CH} \end{smallmatrix} \text{C} \cdot O \cdot \text{C} \begin{smallmatrix} \diagdown \text{CH} \text{---} \text{CO} \\ \diagup \text{CH} \text{:} \text{CMe} \end{smallmatrix} O$, which is a viscid oil. It boils at 172—174° under 16 mm. pressure, gives no reaction with ferric chloride, and is easily hydrolysed by aqueous sodium carbonate; when boiled with acetic anhydride and sodium acetate or pyridine (compare Collie, *Trans.*, 1900, 77, 971), triacetic- δ -lactone forms dehydracetic acid. The action of formaldehyde on triacetic- δ -lactone, in aqueous or alcoholic solution, leads to the formation of *methylenebis-triacetic- δ -lactone*, $O \text{---} \text{CO} \text{---} \begin{smallmatrix} \text{CH} \\ \text{CMe} \end{smallmatrix} \cdot \text{CH}_2 \cdot \begin{smallmatrix} \text{CH} \\ \text{CO} \end{smallmatrix} \text{CO} \cdot O \begin{smallmatrix} \text{CH} \\ \text{CMe} \end{smallmatrix} \text{CO}$, which crystallises in colourless, slender needles, melts and decomposes at 245°, gives a brownish red coloration with ferric chloride in alcoholic solution, and, on titration, with phenolphthalein as indicator, neutralises about $1\frac{1}{2}$ mols. of alkali hydroxide (compare Wolff, *Abstr.*, 1901, i, 283).

C-Carbanilinotriacetic- δ -lactone, $O \text{---} \text{CO} \text{---} \begin{smallmatrix} \text{CH} \\ \text{CMe} \end{smallmatrix} \text{CO} \cdot \text{NHPh}$, formed when molecular proportions of triacetic- δ -lactone and phenylcarbimide

are warmed with sodium acetate, crystallises in thick, colourless prisms, melts at 156° , is easily soluble in aqueous alkali hydroxides, gives an intense yellowish-red coloration with ferric chloride, and forms slightly soluble crystalline *sodium* and *copper* salts. With phenylcarbimide alone, triacetic- δ -lactone forms an *O-derivative*. Dehydracetic acid does not enter into reaction with phenylcarbimide in presence of sodium acetate.

The resemblance of triacetic- δ -lactone to the dihydroresorcinols, and of dehydracetic acid to the *C*-acetyl derivatives of the dihydroresorcinols, supports Feist's formula for dehydracetic acid (Abstr., 1892,



G. Y.

Claisen's Transformation of *O*-Acyl Derivatives of Ethyl Acetoacetate into the Isomeric *C*-Acyl Derivatives. WALTER DIECKMANN and RICHARD STEIN (*Ber.*, 1904, 37, 3392—3396. Compare Claisen and Haase, Abstr., 1901, i, 118).—When warmed for 7 hours with 0.1 gram of sodium and 1 gram of ethyl acetoacetate in absolute ethereal solution, 8 grams of ethyl *O*-acetylacetoacetate yield 1 gram of ethyl diacetoacetate, the action taking place in proportion to the sodium present. When warmed for 15 minutes with 1.1 grams of sodium and 6.5 grams of ethyl acetoacetate, 8.5 grams of ethyl *O*-acetylacetoacetate yield 3 grams of ethyl diacetoacetate. Nine grams of ethyl *O*-acetylacetoacetate, boiled for 16 hours with 0.4 gram of sodium in ethereal solution, yields 1.9 grams of ethyl diacetoacetate and 0.8 gram of ethyl acetoacetate. Eight grams of ethyl *O*-acetylacetoacetate, warmed for $4\frac{1}{2}$ hours with ethyl sodio-benzoylacetate prepared from 1.1 grams of sodium and 9 grams of ethyl benzoylacetate in ethereal solution, yields 2 grams of ethyl diacetoacetate and 3 grams of ethyl *C*-acetylbenzoylacetate. A similar result was obtained by using $1\frac{1}{2}$ mols. of potassium carbonate instead of 1 atom of sodium. These results show that, contrary to Erlenmeyer's view (Abstr., 1901, i, 357), the reaction takes place between a molecule of the *O*-acyl compound and a molecule of the sodio-compound.

Ethyl sodioacetoacetate has no action on ethyl *O*-acetylacetoacetate in ethereal solution, cooled by ice. If an ethereal suspension of ethyl sodioacetoacetate, prepared from 16 grams of ethyl acetoacetate, is poured into twice its volume of ice-cooled acetyl chloride, diluted with ether, it yields, after 20 minutes, 8 grams of ethyl diacetoacetate. This points to the primary formation of the *C*-acetyl derivative by the action of acetyl chloride on the sodio-compound (compare Claisen, Abstr., 1894, i, 31).

G. Y.

Action of Nitrous Acid and its Derivatives on α -Substituted β -Ketonic Esters. Part I. General. Part II. Preparation of α -Oximino-esters and Acids. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1904, [iii], 31, 1049—1055 and 1055—1061. Compare Abstr., 1902, i, 704, 705).—The observations of Meyer and Zublin (Abstr., 1878, 487 and 659), Treadwell and Westenberger (Abstr., 1883, 572), and Ceresole (Abstr., 1882, 1052) on the action of nitrous acid on these esters are reviewed. For the preparation of

the oximino-esters resulting from this reaction, the following methods are recommended. The α -substituted ester is dissolved in twice its weight of sulphuric acid, care being taken to keep the temperature below 0° ; the mixture is kept for two hours at 0° and then nitrosyl-sulphuric acid, dissolved in twice its weight of sulphuric acid, is added very gradually. This mixture is poured on ice and the resulting oximino-compounds extracted with ether. The ethereal solution is washed, first with a solution of sodium carbonate, to remove the oximino-acid simultaneously formed, then with water, and finally the solvent is distilled off and the residue purified by fractional distillation. The yield of ester varies from 85 to 90 per cent., but may be largely replaced by the oximino-acid if the temperature is allowed to rise above 0° , when the β -ketonic ester is dissolved in sulphuric acid. Where it is inconvenient to use sulphuric acid as a solvent, formic or acetic acid may be substituted. When nitrosyl chloride is used in place of "chamber crystals" the reaction is complex and varies with the conditions of the experiment. Nitrous esters in conjunction with sodium alkyloxides may also be employed, but the alkyl group in the nitrite must be the same as that in the ketonic ester used, otherwise substitution may occur. This method is generally applicable, but the yields obtained are less satisfactory and the operation more troublesome than that first described. T. A. H.

Theory of the Transformation of α -Substituted β -Ketonic Esters into α -Oximino-esters. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1904, [iii], 31, 1061—1067. Compare preceding abstract).—When nitrosyl chloride is passed into well-cooled methyl methylacetoacetate, $\text{CHAcMe}\cdot\text{CO}_2\text{Me}$, the odour of acetyl chloride becomes noticeable; if the mixture is then warmed, hydrogen chloride is evolved, and from the residue an oil (b. p. 125° under 14 mm. pressure), which is probably a mixture of methyl α -oximinopropionate with its acetyl derivative, is obtained. Similarly, when dry ammonia is passed into the product obtained by the action of nitrosyl chloride on methyl benzoyl- α -methylacetate, methyl oximinopropionate and benzamide (b. p. 182 — 183° under 1 mm. pressure) are formed.

When α -substituted β -ketonic esters are treated with nitrosyl-sulphuric acid, the reaction proceeds according to the equation:

$$\text{R}\cdot\text{CO}\cdot\text{CHR}'\cdot\text{CO}_2\text{Et} + \text{SO}_2(\text{NO}_2)\cdot\text{OH} =$$

$$\text{R}\cdot\text{CO}_2\text{H} + \text{CR}'(\text{CO}_2\text{Et})\cdot\text{N}\cdot\text{O}\cdot\text{SO}_2\text{OH};$$

thus methyl benzoylmethylacetate, $\text{CHBzMe}\cdot\text{CO}_2\text{Me}$, gives under these conditions benzoic acid and methyl α -oximinopropionate. When the same ester is treated with methyl nitrite in presence of sodium methoxide, the benzoic acid is eliminated as methyl benzoate.

It is remarkable that in all the foregoing reactions α -substituted β -ketonic esters are converted into α -oximino-esters, whereas according to Ceresole (*Abstr.*, 1882, 1052) the action of nitrous acid on these esters gives rise to the monoxime of the α -diketone. This difference is probably due to the fact that in the reactions now described the β -ketonic esters are converted by the solvents employed into derivatives of the enolic forms of the esters, and it is suggested that the

solutions in sulphuric acid contain acid sulphates of these enolic forms, for example, $\text{HO}\cdot\text{SO}_2\cdot\text{O}\cdot\text{CR}:\text{CR}'\cdot\text{CO}_2\text{H}$. Adopting this explanation, the following rule may be given. *When the enolic form of an α -substituted β -ketonic ester is treated with nitrous acid or its derivatives it is converted into an α -oximino-ester.* T. A. H.

α -Oximino-derivatives of Homologues of Pyruvic Acid and its Esters. RENÉ LOCQUIN (*Bull. Soc. chim.*, 1904, [iii], 31, 1068—1075. Compare Bouveault and Locquin, *Abstr.*, 1902, i, 704, 705).—The following compounds were prepared by the action of nitrosyl-sulphuric acid on the appropriate α -alkylacetoacetic ester as described in the preceding abstracts.

Methyl α -oximinopropionate, $\text{NOH}:\text{CMe}\cdot\text{CO}_2\text{Me}$, furnishes an *acetyl* derivative which melts at 42° and boils at 126° under 14 mm. pressure. The *butyryl* derivative, obtained as a liquid by the action of butyryl chloride on the oxime, distils at 153 — 155° under 16 mm. pressure, but could not be obtained pure. The *benzoyl* derivative melts at 103° (corr.), boils and decomposes at about 190° under 12 mm. pressure, and is resolved into its generators by solution in sulphuric acid at 0° . α -Oximinobutyric acid, $\text{NOH}:\text{CEt}\cdot\text{CO}_2\text{H}$, obtained by hydrolysing the ethyl ester (Lepereq, *loc. cit.*, and Bouveault and Locquin, *Abstr.*, 1902, i, 704), crystallises in colourless needles and melts at 169 — 170° (corr.) (compare Hantzsch and Wild, *Abstr.*, 1896, i, 285).

Ethyl α -oximinoisovalerate, $\text{NOH}:\text{CPr}^\beta\cdot\text{CO}_2\text{Et}$, melts at 57° and boils at 129° under 13 mm. pressure (compare Bouveault and Wahl, *Abstr.*, 1902, i, 137); the corresponding acid volatilises and decomposes at 150° , but melts on the mercury-bath at 171 — 172° (corr.).

Ethyl α -oximinovalerate, $\text{NOH}:\text{CPr}^\alpha\cdot\text{CO}_2\text{Et}$, melts at 48° and boils at 144 — 145° under 16 mm. pressure. *isoButyl α -oximinovalerate*, $\text{NOH}:\text{CPr}^\alpha\cdot\text{CO}_2\cdot\text{C}_4\text{H}_9$, prepared from *isobutyl* propylacetoacetate (sp. gr. 0.954 at $0^\circ/4^\circ$ and b. p. 115 — 116° under 13 mm. pressure), boils at 152° under 15 mm. pressure and melts at 16° . With this compound there is formed some *isobutyl α -ketovalerate*. α -Oximinovaleric acid forms small, white crystals, melts and decomposes at 155° (corr.), and sublimes at 145° (compare Fürth, *Abstr.*, 1884, 42). The metallic salts are soluble in water. *Ethyl α -oximinoisohexanoate* melts at 60° and boils at 142° under 12 mm. pressure. The corresponding acid (Miller and Flochl, *Abstr.*, 1893, i, 502) melts at 152 — 154° (corr.); it furnishes a crystalline *silver* salt. *Ethyl α -oximinoisohexanoate*, prepared from ethyl *isoamyl*acetoacetate (*Abstr.*, 1904, i, 646), boils at 156° under 16 mm. pressure and has sp. gr. 0.911 at $0^\circ/4^\circ$. The corresponding acid melts at 163 — 164° (corr.); the *sodium* salt is crystalline. α -Oximinodecic acid (methylhexylpyruvic acid oxime) crystallises from a mixture of ether and light petroleum, melts at 89 — 90° (corr.), and is soluble in organic liquids (*Abstr.*, 1902, i, 704). T. A. H.

Electrolytic Reduction of Carboxylic Acids and their Esters in Sulphuric Acid Solution. JULIUS TAFEL and GUSTAV FRIEDRICHS (*Ber.*, 1904, 37, 3187—3191).—Oxalic acid is reduced

electrolytically in presence of sulphuric acid to glyoxylic acid, the change being nearly quantitative. Other dicarboxylic acids, such as malonic, succinic, and tartaric acids, as well as most monocarboxylic acids, remain unaltered. On the other hand, the esters of oxalic, malonic, acetoacetic, benzoic and phthalic acids are all easily reduced electrolytically: thus ethyl benzoate is reduced to benzyl ethyl ether, boiling at 187—189°, and methyl benzoate to benzyl methyl ether boiling at 169°, both under 732 mm. pressure. In the case of ethyl oxalacetate and ethyl benzoylacetate, apparently only the keto-group is attacked, as only 2 atoms of hydrogen are used. Ethyl oxalate requires 4 atoms of hydrogen in aqueous and only 2 in alcoholic solution.

E. F. A.

Aqueous Solutions of Magnesium Oxalate. FRIEDRICH KOHLRAUSCH and FRANZ MYLIUS (*Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 1223—1227).—Solutions of magnesium oxalate were prepared by saturating an oxalic acid solution with magnesium hydroxide, filtering, and neutralising by means of a drop of oxalic acid. By this means a 10 per cent. solution could be prepared, that is, a solution of about 300 times the concentration of the saturated solution of $\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. The solution, however, soon becomes turbid. A solution of concentration 1.1753 per cent., although 30 times as concentrated as the saturated solution, is sufficiently stable to allow its conductivity to be determined, as after a fortnight it is still 1.5 times super-saturated. The conductivities from 0.209 *N* to 0.0000266 *N* solutions were determined by diluting such a solution. The limiting value calculated from the migration velocities agrees well with that deduced from the determinations. The equivalent conductivity sinks very rapidly with increase of concentration, whilst the temperature-coefficient is also very low. The author considers that these results indicate the formation of molecular complexes in the solutions.

L. M. J.

Electrolysis of Dicarboxylic Organic Acids: Glutaric Acid. L. VANZETTI (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 112—120).—On electrolysing a 20 per cent. solution of potassium glutarate in an atmosphere of carbon dioxide, the voltage being 10 and the current 2—2½ amperes, the gas formed was found to be propylene; no trimethylene was obtained, although this might have been expected.

T. H. P.

Complex Compounds of Molybdic Acid and of Tungstic Acid with Organic Acids. HERMANN GROSSMANN and HANS KRÄMER (*Zeit. anorg. Chem.*, 1904, 41, 43—60. Compare Abstr., 1903, i, 549).—From the determinations of electrical conductivity quoted, it appears that in solutions which contain sodium molybdate, Na_2MoO_4 (1 mol.), or sodium tungstate, Na_2WO_4 (1 mol.), mixed with oxalic acid (1 mol.), tartaric acid (1 mol.), or malic acid (1 mol.), normal salts of dibasic acids are produced, which in dilute solution suffer considerable hydrolytic dissociation; this hydrolytic dissocia-

tion is more marked with the complex molybdates than with the complex tungstates. The disodium citrates behaved similarly.

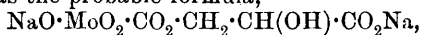
Gernez' view that tartaric acid and malic acid form various complexes with sodium molybdate and sodium tungstate according to the amount of the latter salts present does not hold for the concentrations studied by the authors.

It is very probable that, in the cases examined, the trioxides of molybdenum and of tungsten are respectively united with the carboxyl groups of the organic acids.

The speed of the anion is diminished by the introduction of the trioxide of molybdenum or tungsten.

Mixtures containing normal tungstate (1 mol.) and acid (2 mols.) were also examined; the salts formed undergo decomposition at moderate dilutions.

The malate has the probable formula,



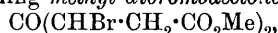
and the tartrate, $\text{NaO} \cdot \text{MoO}_2 \cdot \text{CO}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2 \text{Na}.$

A. McK.

***β*-isoMalic Acid.** GERRIT H. COOPS (*Chem. Centr.*, 1904, ii, 641; from *Chem. Weekblad.*, 1, 535—541).—*β*-isoMalic acid, $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{H})_2$, obtained by hydrolysing the oily ester, $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{Et})_2$, produced from ethyl sodiomalonate and ethyl trioxymethylene chloride, is a syrup, decomposing on heating into acrylic acid, and yielding amorphous insoluble *calcium* and *copper* salts.

W. D. H.

Symmetrical Ethyl Ketopentadienedicarboxylic Acid. FRITZ STRAUS (*Ber.*, 1904, 37, 3293—3298).—Bromine reacts with a chloroform solution of methyl acetonediacetate (hydrochelidonate; Volhard, *Abstr.*, 1890, 30) yielding *methyl dibromoacetonediacetate*,



which crystallises from methyl alcohol in colourless prisms melting at 58°. When heated with quinoline, hydrogen bromide is evolved and *methyl ketopentadienedicarboxylate*, $\text{CO}(\text{CH}:\text{CH} \cdot \text{CO}_2\text{Me})_2$, is formed; this crystallises from ethyl acetate in yellow plates melting at 169—169·5°, and yields a *tetrabromide*, which crystallises in small, colourless needles melting and decomposing at 207°. When exposed to sunlight, either in the dry form or in solution, the yellow ester is transformed into a colourless isomeride, which crystallises from ethyl acetate and melts and decomposes at 240—241°.

Ethyl dibromoacetonediacetate forms colourless needles melting at 48·5—49°; *ethyl ketopentadienedicarboxylate* crystallises in yellow prisms and melts at 49·5—50°; the *tetrabromide* melts at 171—172°. *Ketopentadienedicarboxylic acid*, obtained by the hydrolysis of the ethyl ester with 75 per cent. sulphuric acid, crystallises from water in yellow plates decomposing at 230°.

The ethyl ester combines with hydrogen chloride, yielding a compound, $\text{C}_{11}\text{H}_{16}\text{O}_5\text{Cl}_2$, which crystallises from alcohol in colourless needles melting at 60—75°. Heating with quinoline eliminates hydrogen chloride from this compound, and the original unsaturated acid is obtained.

An ethereal solution of the ester does not yield a precipitate with

mercuric chloride, and on removal of the mercury an oil is obtained which slowly solidifies. J. J. S.

Behaviour of Formaldehyde towards Various Solvents. KÖRBER (*Chem. Centr.*, 1904, ii, 585—586; from *Pharm. Zeit.*, 49, 608).—When formaldehyde is passed into dry chloroform, which is free from acid, at about 130°, diformaldehyde, $C_2H_4O_2$, separates in flakes and partly sublimes, whilst another form of the aldehyde is left in the mother liquor. The action is enormously increased by exposure to sunlight. Diformaldehyde is readily soluble in a small quantity of water; when left in the chloroform mother liquor, it is only very slowly converted by the action of direct sunlight into a form which is insoluble in water. E. W. W.

Acetylacetone-dioxime from Sorbic Acid. FRANZ FEIST (*Ber.*, 1904, 37, 3316).—Acetylacetonedioxime (Harries and Haga, *Abstr.*, 1899, i, 562) is formed when sorbic acid is heated with a methyl-alcoholic solution of free hydroxylamine for five hours at 100°, and may be isolated by evaporation of the solution under reduced pressure, solution in water, and extraction with ether. The oxime readily reduces Fehling's solution, and hence probably exists as the tautomeric hydroxylamino-oxime, $OH \cdot NH \cdot CMe : CH \cdot CMe : N \cdot OH$. J. J. S.

Final Products of the Hydrolysis of Starch by Oxalic Acid, with special reference to Dierssen's (Lintner's) "*iso*Maltose." FRITZ GRÜTERS (*Zeit. angew. Chem.*, 1904, 17, 1169—1179).—According to Lintner, maltose is not formed during the hydrolysis of starch by oxalic acid, the products successively formed being amyloextrin, erythroextrin I, erythroextrin II_a, erythroextrin II_β, achroodextrin I, achroodextrin II, *isomaltose*, and dextrose, whilst during the hydrolysis of starch by diastase the products are amyloextrin, erythroextrin I, achroodextrin I, achroodextrin II, *isomaltose*, and maltose. Since Lintner's arguments for the existence of "*isomaltose*" are largely based on his conclusion that in the hydrolysis of starch by oxalic acid no maltose is produced, but a biose, which forms an osazone with properties corresponding with Fischer's *isomaltosazone*, the author has made a further study of the hydrolysis of starch by oxalic acid.

Lintner's conclusions as to the existence of "*isomaltose*" were confirmed by Dierssen (*Abstr.*, 1903, i, 321). The author agrees with Dierssen that starch, free from sucrose, yields by hydrolysis with oxalic acid traces of *d*-fructose.

Potato starch, which was free from sugar, was hydrolysed by oxalic acid and the product submitted to an exhaustive fractionation by dilute alcohol. It is concluded that "*isomaltose*" with $[\alpha]_D^{140}$ (Lintner) was not present, and that the products obtained by Lintner and by Dierssen probably contained a considerable amount of some substance which was not a carbohydrate.

From one of the fractions with $[\alpha]_D^{155}$, a carbohydrate having $[\alpha]_D^{163}$ was obtained by further fractionation. It was free from sugar, since no osazone could be formed, and it gave no coloration with iodine.

It is designated as achroodextrin IV or maltodextrin γ (compare Ling and Baker, *Trans.*, 1897, 71, 508). It does not crystallise. It is fermentable by bottom yeast, although not very readily. Its specific rotation is slightly lowered by the action of diastase. Its reducing power $R = 61$ per cent. maltose.

Lintner and Dierssen's "isomaltose" is in no way different from a mixture of maltose and dextrin with a small amount of decomposition products.

The products of the hydrolysis of starch by oxalic acid are, according to the author, achroodextrin I, achroodextrin II, maltodextrin γ , maltose, dextrose (*d*-fructose), whilst with diastase the products are achroodextrin I, maltodextrin α , maltodextrin β , maltose (dextrose).

A. McK.

Carbohydrate with High Molecular Weight from the Roots of *Heteropteris Pauciflora*. CARL MANNICH (*Chem. Centr.*, 1904, ii, 347; from *Ber. deut. pharm. Ges.*, 14, 302—308).—The carbohydrate, *heteropterin*, $C_6H_{10}O_5 \cdot \frac{1}{6}H_2O$, resembles starch in appearance, is extremely hygroscopic, and has a slight, but not sweet, taste. It begins to soften when heated at 140° and becomes viscous at 160° ; at 195° , it begins to froth. It dissolves in water, has $[\alpha]_D -40.98^\circ$ at 20° in 6.068 per cent. aqueous solution, reduces Fehling's solution very slightly, reduces ammoniacal silver solutions when boiled for a short time, and gives a white precipitate with baryta. With phenylhydrazine, it yields only a minute amount of osazone. It does not ferment. When hydrolysed, it yields only lævulose.

N. H. J. M.

Acetyl Derivative of Cellulose. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 153350).—The ordinary acetylcellulose is insoluble in alcohol. A soluble acetylcellulose is obtained by the action of acetic anhydride on hydrocellulose in the presence of a large quantity of concentrated sulphuric acid. The concentrated alcoholic solution forms a solid jelly when cold, but becomes liquid on warming. Water precipitates the acetyl compound from its solution in alcohol, acetic acid, or acetone.

C. H. D.

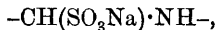
Alkylamines containing Fluorine. FRÉDÉRIC SWARTS (*Bull. Acad. Roy. Belg.*, 1903, 6, 762—801).—When heated under pressure at 125 — 145° with alcoholic ammonia, bromodifluoroethane, $CHF_2 \cdot CH_2Br$, is converted into a mixture of two amines, difluoroethylamine and tetrafluorodiethylamine, which can be separated by means of their oxalates or hydrochlorides.

Difluoroethylamine, $CHF_2 \cdot CH_2 \cdot NH_2$, is a colourless liquid with an ammoniacal odour, boiling at 67.5 — 67.8° (corr.) under 757 mm. pressure, has a sp. gr. 1.175 at 11.9° , absorbs carbon dioxide, and is miscible with water in all proportions. The *hydrochloride* forms colourless crystals melting at 183° , easily soluble in water, but sparingly so in cold alcohol; the *sulphate* crystallises in plates; the normal *oxalate* forms large, colourless crystals and the *platinichloride* brown crystals. *Difluoroethylurethane*, $CHF_2 \cdot CH_2 \cdot NH \cdot CO_2Et$, forms colourless platelets melt-

ing at 37.6° and boiling at 184° . *Diffuoroethylnitroamine* melts at 22.4° and boils at 111 — 112° ; its *ammonium* salt crystallises in needles melting at 91° , and the sodium salt also forms needles.

Tetrafluorodiethylamine, $\text{NH}(\text{CH}_2\cdot\text{CHF}_2)_2$, is a colourless liquid with an odour like acetamide; it boils at 124.4° (corr.) under 755 mm. pressure, has a sp. gr. = 1.304 at 16.5° , and forms a *hydrochloride* crystallising in needles which melt at 171° and are easily soluble in alcohol. The *sulphate* crystallises in prisms. *Tetrafluorodiethylnitrosoamine*, $\text{NO}\cdot\text{N}(\text{CH}_2\cdot\text{CHF}_2)_2$, forms a pale yellow liquid boiling at 178.6° .
E. F. A.

The Doubly Linked Carbon Nitrogen System $>\text{C}:\text{N}$. LOUIS HENRY (*Bull. Acad. Roy. Belg.*, 1904, 6, 741—754).—Compounds containing the group $\cdot\text{CH}:\text{N}\cdot$ are able to unite with either sodium hydrogen sulphite or hydrogen cyanide. Thus, with sodium hydrogen sulphite, crystalline products are obtained of the type

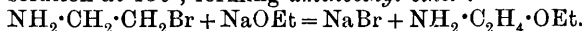


which further react with acids or bases just as the hydrogen sulphite compounds of aldehydes and ketones do. Thus, from *isoamylheptylideneimine*, a sparingly soluble compound, $\text{C}_6\text{H}_{13}\cdot\text{CH}(\text{SO}_3\text{Na})\cdot\text{NH}\cdot\text{C}_5\text{H}_{11}$, crystallising in plates, is obtained. *Ethylethylideneimine* (boiling at 48°) combines with hydrogen cyanide forming *α -cyanodiethylamine*, $\text{CH}_3\cdot\text{CH}(\text{CN})\cdot\text{NH}\text{Et}$, boiling at 153 — 154° ; *propylpropylideneimine*, prepared from propylamine and propaldehyde and boiling at 101 — 102° , forms *α -cyanodipropylamine*, $\text{C}_3\text{H}_7\cdot\text{CH}(\text{CN})\cdot\text{NH}\cdot\text{C}_3\text{H}_7$, boiling at 176 — 177° , whilst *isobutylethylideneimine*, which boils at 90 — 91° , forms *isobutyl- α -cyanoethylamine*, $\text{CH}_3\cdot\text{CH}(\text{CN})\cdot\text{NH}\cdot\text{C}_4\text{H}_9$, which distils at 168 — 169° . These nitrilimines are hydrolysed by acids to the corresponding carboxylic acids; bases convert them into hydrogen cyanide, aldehyde, and primary amine. *Cyanotrimethylamine*, $\text{NMe}_2\cdot\text{CH}_2\cdot\text{CN}$, obtained by the action of hydrogen cyanide and formaldehyde on dimethylamine, melts at 139° ; *dimethyl- α -cyanoethylamine*, $\text{NMe}_2\cdot\text{CHMe}\cdot\text{CN}$, melts at 144° , whilst *dimethyl- α -cyanoisopropylamine*, $\text{NMe}_2\cdot\text{CMe}_2\cdot\text{CN}$, melts at 152° .
E. F. A.

Synthesis of Dimethylaminoethyl Ether. LUDWIG KNORR (*Ber.*, 1904, 37, 3504—3505).—Iodoether and dimethylamine combine together at 150° to form the hydriodide of dimethylaminoethyl ether: $\text{NHMe}_2 + \text{I}\cdot\text{C}_2\text{H}_4\cdot\text{O}\cdot\text{C}_2\text{H}_5 = \text{NHMe}_2\cdot\text{C}_2\text{H}_4\cdot\text{O}\cdot\text{C}_2\text{H}_5$.

The same base may be synthesised by heating an alcoholic solution of chloroethyldimethylamine hydrochloride and sodium ethoxide at 150 — 160° : $\text{NMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl} + \text{NaOEt} = \text{NMe}_2\cdot\text{C}_2\text{H}_4\cdot\text{O}\cdot\text{C}_2\text{H}_5 + \text{NaCl}$. The product is in both cases identical with the base obtained from methylmorphinemethine, thebaine methiodide, or codeinone methiodide (this vol., i, 916).
C. H. D.

Aminoethyl Ether. LUDWIG KNORR (*Ber.*, 1904, 37, 3506—3507).—Bromoethylamine hydrobromide reacts with sodium ethoxide in alcoholic solution at 150° , forming *aminoethyl ether*:



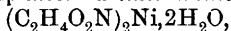
After distilling over barium oxide, the ether boils at 108—109° under 760 mm. pressure, and dissolves readily in water or other solvents; it reacts strongly alkaline, and has a powerful amine-like odour. The salts are readily soluble and crystallise with difficulty. The *aurichloride* separates as an oil, which slowly crystallises. C. H. D.

Betaine Periodide. VL. STANĚK (*Zeit. Zuckerind. Böhm.*, 1904, 28, 578—583. See this vol., ii, 790).

Copper Nickel Salts of some Amino-acids. GIUSEPPE BRUNI and C. FORNARA (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 26—30).—The copper salts of the amino-acids differ from most others in having a bluish-violet colour similar to that of the cuprammonium salts.

The copper salts prepared and examined by the authors were those of glycine, α -alanine, α -aminoisobutyric acid, leucine, aspartic acid, asparagine, and *o*-, *m*-, and *p*-aminobenzoic acids. Except in the case of the last three acids, the copper salts cannot conveniently be prepared by dissolving copper oxide in the acid, but are readily obtainable by mixing the calculated quantity of copper sulphate solution with a cold solution of barium hydroxide, and adding an excess of the pasty mixture of barium sulphate and cupric hydroxide formed to an aqueous solution of the amino-acid. The copper salts of the aminobenzoic acids have a green colour, the intensity of which increases from the ortho- to the para-derivative, and copper aspartate is azure-blue, tending towards violet; the salts of all the α -amino-fatty acids have the characteristic violet colour, which is scarcely intensified by the addition of ammonia to their aqueous solutions. All these salts resemble the cuprammonium compounds in not yielding precipitates with potassium hydroxide, sodium carbonate, or potassium ferrocyanide, or thiocyanate; hydrogen sulphide or an alkali sulphide precipitates cupric sulphide, but only incompletely, whilst potassium cyanide decolorises the solutions. This behaviour shows that in solutions of these salts copper ions are present only in extremely small quantity, so that even with an excess of reagent it is impossible to exceed the relative solubility product.

The corresponding nickel salts, previously unknown, were prepared by treating a solution of the amino-acid with a paste of nickel hydroxide and barium sulphate. *Nickel aminoacetate*,

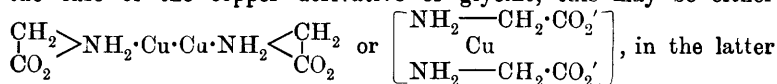


forms minute, pale blue crystals, moderately soluble in water. *Nickel α -aminopropionate*, $(\text{C}_3\text{H}_6\text{O}_2\text{N})_2\text{Ni}\cdot 4\text{H}_2\text{O}$, is very similar to the aminoacetate. The nickel salts of the three aminobenzoic acids are green and practically insoluble in water. The aspartate is also green, but moderately soluble in water, but the asparagine derivative is pale blue and gives a dark blue solution. In solutions of these nickel salts, the concentration of the metallic ions seems to be greater than in solutions of the corresponding copper salts, because they give precipitates with alkali sulphides and also with alkali hydroxides and carbonates; they do not, however, yield precipitates with potassium ferrocyanide or sodium phosphate. The nickel salt of asparagine resembles more

the metallo-ammonium compounds, as it is not precipitated by alkali hydroxides or carbonates, and only incompletely by alkali sulphides.

In order that these salts may exhibit the behaviour of the metallo-ammonium salts, it seems necessary that the amino-group should occupy the α -position.

These salts may have either one of two structures in solution. In the case of the copper derivative of glycine, this may be either



case, the atom of copper being surrounded by two NH_2 groups and two negative radicles, thus forming a neutral and non-ionising complex. T. H. P.

Hydroxylamines. FELIX HAASE and RICHARD WOLFFENSTEIN (*Ber.*, 1904, 37, 3228—3238).—Piperidine oxide and benzyl chloride react in cold ethereal solution, forming benzylpiperidine oxide; on reduction with zinc and hydrochloric acid, this forms benzylpiperidine, of which the *hydrochloride* melts at 178° and the *platinichloride* at 191 — 193° . 1-Methylpiperidine oxide forms a picrate melting at 176 — 178° and a *platinichloride* melting at 188° . The *methiodide* is reduced by zinc and hydrochloric acid to 1-methylpiperidine.

Diethylhydroxylamine and carbon disulphide unite to form diethylamine diethyldithiocarbamate, melting at 83° and identical with the product obtained from diethylamine and carbon disulphide.

Dibenzylamine dibenzylidithiocarbamate, prepared from dibenzylhydroxylamine in the same manner, melts at 82.5° . Carbanilinopiperidine oxide, prepared by the interaction of phenylcarbimide and piperidine oxide, melts at 105 — 106° and forms a *p-nitrophenylhydrazone* melting at 211° . Carbanilindibenzylhydroxylamine forms a *p-nitrophenylhydrazone*, crystallising in yellow needles from ether and melting at 209° . E. F. A.

Electrolytic Preparation of Potassium Cyanate. EMANUELE PATERNO and E. PANNAIN (*Gazzetta*, 1904, 34, ii, 152—155).—The most favourable conditions for the electrolytic oxidation of potassium cyanide to cyanate are: (1) The concentration of the cyanide to be from 4 to 6 gram-mols. per litre. (2) The presence of 1 gram-mol. of potassium hydroxide per litre. (3) An *E.M.F.* of 4 to 6 volts. (4) An anodic current density of from 1 to 4 amperes per sq. dm. (5) The electrolyte to be mixed by agitating the anode. Under these conditions, and if the electrolysis is sufficiently prolonged, almost the whole of the cyanide is converted into cyanate, part of which crystallises out during the electrolysis. T. H. P.

Oxidation of Thiocyanic Acid and its Salts by Hydrogen Peroxide. JOSEPH H. KASTLE and CLAUDE R. SMITH (*Amer. Chem. J.*, 1904, 32, 376—385).—Kastle and Loevenhart (*Abstr.*, 1903, ii, 415, 537) have shown that ammonium thiocyanate is readily oxidised by hydrogen peroxide with formation of ammonium hydrogen sulphate and hydrogen cyanide. This reaction has now been closely studied.

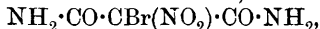
The influence of small quantities of various oxygen carriers, namely, manganese chloride, manganese dioxide, silver nitrate, potassium chloride, bromide, and iodide, copper sulphate, nitrate, and acetate, ferrous sulphate, mercuric chloride, and platinum black, on the action of hydrogen peroxide on thiocyanic acid and its potassium and barium salts has been determined, and the results are tabulated. It is found that, both in presence and absence of oxygen carriers, thiocyanic acid is more rapidly oxidised than either of its salts, and that the oxidation of both the acid and its salts is greatly accelerated by various substances, particularly by those which effect the decomposition of hydrogen peroxide, such as chrome alum, copper sulphate and nitrate, and ferrous sulphate. Nickel and cobalt salts accelerate the oxidation of thiocyanic acid, but have little influence on the oxidation of the salts. Platinum black, manganese dioxide, and potassium iodide have practically no effect on the rate of oxidation.

The oxidation of thiocyanic acid by hydrogen peroxide takes place according to the following equation: $\text{HCNS} + 3\text{H}_2\text{O}_2 = \text{HCN} + \text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$. The reaction was studied by van't Hoff's method and appears to be one of the third order. The oxidation probably takes place in two stages: (1) $\text{HCNS} + 2\text{H}_2\text{O}_2 = \text{HCN} + 2\text{H}_2\text{O} + \text{SO}_2$; and (2) $\text{SO}_2 + \text{H}_2\text{O}_2 = \text{H}_2\text{SO}_4$. The velocity of the reaction was determined both with thiocyanic acid and its potassium salt. The results are tabulated and show that it is possible to obtain fairly constant values for the coefficient of velocity of a reaction of the third order. It has also been observed that a rise of temperature of 10° nearly doubles the velocity of the reaction.

E. G.

Action of Nitrous Acid on the Amide of Malonic Acid and its Homologues. I. FLORIAN RATZ (*Monatsh.*, 1904, 25, 687—744. Compare this vol., i, 298).—When warmed with concentrated hydrochloric acid, nitromalonamide is hydrolysed, almost quantitatively, to carbon dioxide, ammonia, formic acid, and hydroxylamine.

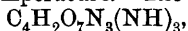
The action of bromine on nitromalonamide suspended in water leads to the formation of *bromonitromalonamide*,



which crystallises in slender, white needles, melts at $131\text{--}132^\circ$, is easily soluble in acetone or methyl alcohol, and, when boiled with water, is decomposed with evolution of bromonitromethane. With aqueous silver nitrate solution, in presence of very dilute alkali hydroxides or ammonia, it yields a white precipitate consisting of a mixture of silver cyanate and the silver salt of nitromalonamide. When heated in a sealed tube for half an hour with alcohol, or for a few minutes with alcohol in presence of a trace of sodium acetate or of an alkali hydroxide, bromonitromalonamide yields nitromalonamide, dibromonitroacetamide, and a small amount of ethyl alllophanate. The *ammonium* salt of ethyl nitromalonate (Franchimont and Klobbie, *Abstr.*, 1889, 1143) crystallises in yellow, hexagonal plates and melts and decomposes at $152\text{--}153^\circ$. When heated with aqueous or alcoholic ammonia in a sealed tube at 100° , it is converted into nitroacetamide and urethane. The reaction takes place very slowly, part of the ethyl nitromalonate remaining unchanged after three hours' heating.

When boiled with water and one molecular proportion of ammonia, nitromalonamide yields the same products as when it is boiled with water alone, but when boiled with water in presence of an excess of ammonia ($25\text{NH}_3 : \text{C}_3\text{H}_5\text{O}_4\text{N}_3$) it yields nitroacetamide and carbamide. Nitroacetamide is isolated as its *ammonium* salt, $\text{C}_2\text{H}_3\text{O}_3\text{N}_2 \cdot \text{NH}_4$, which crystallises in prismatic needles, melts and decomposes at $146-147^\circ$, and evolves hydrogen cyanide on prolonged warming in concentrated aqueous solution. With silver nitrate or lead acetate, the aqueous solution gives precipitates consisting of microscopic, prismatic needles; the green precipitate formed on addition of copper acetate is composed of stellate clusters of crystals; with ferrous and ferric salts, amorphous yellow precipitates are formed; the silver salt, $\text{C}_2\text{H}_3\text{O}_3\text{N}_2 \cdot \text{Ag}$, explodes when heated. *Nitroacetamide*, $\text{NO}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$, obtained by treating the silver salt with a slight excess of hydrochloric acid, crystallises in slender needles, decomposes at $97-98^\circ$, and is easily soluble in water, acetone, or methyl or ethyl alcohols, less so in chloroform, ether, or benzene; its acid nature is less pronounced than that of nitromalonamide. As when nitromalonamide (1 part) is boiled for 30-45 minutes with water (10 parts) and potassium hydroxide (1.52 parts) the products obtained are nitroacetamide and potassium cyanate, the production of carbamide by the action of aqueous ammonia or nitromalonamide is due probably to the intermediate formation of ammonium cyanate.

When boiled with dilute alkali hydroxides or dilute acids, 1 mol. of nitroacetamide slowly yields ammonia, equivalent to 1 atom of nitrogen. With alkali hydroxides, the hydrolysis is slightly more rapid than is that of cyanic acid. If a normal solution of nitroacetamide, to which 5 mols. of potassium hydroxide have been added, is distilled with a current of steam, 1 atom of nitrogen is evolved as ammonia in 30 minutes. From the distillation residue, when cooled, neutralised, and extracted with ether, there is obtained a complex substance, $\text{C}_4\text{H}_5\text{O}_7\text{N}_3 \cdot \frac{3}{2}\text{H}_2\text{O}$, which crystallises in needles and melts with evolution of a gas. It is very hygroscopic; the aqueous solution gives a strong acid reaction and liberates carbon dioxide from potassium carbonate, but gives no precipitation with silver nitrate. It is so unstable that it commences to decompose and evolve a gas in a vacuum at the ordinary temperature. The *ammonium* salt,



is a white, crystalline powder; the explosive *silver* salt forms microscopic clusters of yellow crystals and quickly blackens, even in absence of light. If nitroacetamide in $N/2$ solution is heated to 100° and potassium hydroxide, 8 mols., slowly added, methazonic acid is obtained. This acid is also obtained directly from the complex substance.

When warmed with concentrated hydrochloric acid, nitroacetamide is hydrolysed, more easily than nitromalonamide, to ammonia, carbon dioxide, formic acid, hydroxylamine, and a trace of oxalic acid.

Dibromonitroacetamide, $\text{NO}_2 \cdot \text{CBr}_2 \cdot \text{CO} \cdot \text{NH}_2$, formed by the action of bromine on nitroacetamide in aqueous solution, crystallises from hot water in long needles, from benzene in glistening, fatty leaflets, and is easily soluble in methyl or ethyl alcohol, acetone, or ether. The dibromo-compound is partly decomposed on prolonged boiling with

absolute alcohol, the decomposition being greatly accelerated by the presence of a trace of an alkali hydroxide or of sodium acetate. When triturated with water and treated with potassium hydroxide or ammonia, dibromonitroacetamide yields an oil which has a suffocating odour, is volatile in a current of steam, and gives analytical results corresponding with a mixture of tribromonitro- and dibromonitromethane. The dibromonitromethane at first formed is further brominated, probably at the expense of unchanged dibromonitroacetamide.

Bromonitroacetamide, $\text{NO}_2\cdot\text{CHBr}\cdot\text{CO}\cdot\text{NH}_2$, is formed by the action of potassium hydroxide (not more than $1\frac{1}{2}$ mols.) on the dibromocompound in very dilute solution and in presence of a bromine-absorbent such as carbamide, and treatment of the resulting *potassium* salt, $\text{C}_2\text{H}_2\text{O}_3\text{N}_2\text{BrK}$, with dilute sulphuric acid. It crystallises in white needles, melts at 79° , and contains a small amount of nitroacetamide.

The action of methyl iodide on silver nitroacetamide, suspended in methyl alcohol, leads to the formation of :

(1) A small amount of nitromethylacetamide, $\text{C}_2\text{H}_3\text{O}_3\text{N}_2\text{Me}$, which crystallises in long, white needles, melts and decomposes at 112° , and loses half its nitrogen as ammonia when boiled with dilute aqueous alkali hydroxides, but much more slowly than does nitroacetamide. If boiled with dilute sulphuric acid and thereafter distilled with excess of potassium hydroxide, it further loses 21 per cent. of the remaining nitrogen. The small yield of the methyl derivative might be due to the silver salt of nitroacetamide being a mixture of the salts of two stereoisomeric *isonitro*-compounds. To test this, ammonium nitroacetamide in aqueous solution was precipitated in eleven fractions by silver nitrate. The first fractions were white, the later yellow; both the white and the yellow fractions have the composition $\text{C}_2\text{H}_3\text{O}_3\text{N}_2\text{Ag}$; the solubility of the white salt is 1 part in 306 of water, that of the yellow salt is 1 part in 151 of water. Both salts give the same nitroacetamide on treatment with hydrochloric acid.

(2) The second *product* from the methylation of silver nitroacetamide is a crystalline substance which melts and decomposes at $250\text{--}255^\circ$, is only sparingly soluble in boiling methyl or ethyl alcohol, and, when treated with potassium hydroxide in aqueous solution, loses 25 per cent. of its nitrogen as ammonia and yields the *potassium* salt of an acid. This salt is almost insoluble in alcohol; the *silver* salt, $\text{C}_4\text{H}_4\text{O}_5\text{N}_3\text{Ag}$, crystallises in needles and explodes when heated. The *acid*, $\text{C}_4\text{H}_5\text{O}_5\text{N}_3$, obtained from the silver salt by the action of hydrochloric acid, crystallises in small, compact nodules, melts and decomposes at 101° , is easily soluble in water or alcohol, and forms characteristic crystalline insoluble salts with *silver*, *lead*, *copper*, *barium*, and *potassium*.

When reduced with tin and hydrochloric acid, ammonium nitroacetamide yields ammonium chloride and a white, hygroscopic, crystalline substance which reduces Fehling's solution at the ordinary temperature and, with copper acetate, forms a precipitate consisting of slender needles. No aminoacetic acid could be detected amongst the products. Even after energetic reduction with excess of tin and hydrochloric acid, and by warming with stannous chloride and hydrochloric acid, no trace of

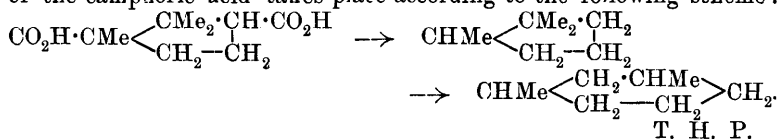
methylaniline and not more than 1 mol. of ammonia per mol. of nitroacetanilide could be detected. G. Y.

Solubility and Polymerisation of Cyanogen. Reactions between Cyanogen and Potassium Cyanide. Thermochemical Studies on the Solution and Polymerisation of Cyanogen. The Slow Oxidation of Cyanogen and Cyanides by Free Oxygen. MARCELLIN BERTHELOT (*Ann. Chim. Phys.*, 1904, [viii], 3, 145—181).—A résumé of work already published (compare this vol., i, 720, 721, 793). M. A. W.

Preparation of Cyanides from Ferrocyanides. GROSSMANN'S CYANIDE PATENTS SYNDICATE (D.R.-P. 153358. Compare this vol., i, 562).—In the regeneration of potassium ferrocyanide from "Everitt's salt," obtained as a by-product in the preparation of hydrocyanic acid from ferrocyanides, alkali carbonate may replace the alkali hydroxide. Little more than the theoretical quantity of alkali carbonate is required, and on passing a current of air the iron is precipitated as ferric hydroxide. C. H. D.

A Reaction of Potassium Ferrocyanide. ALEXANDER GUTBIER (*Zeit. anorg. Chem.*, 1904, 41, 61—62).—When an aqueous solution of potassium ferrocyanide is warmed with a freshly-prepared aqueous solution of phenylhydrazine hydrochloride, the liquid assumes first a brownish-red and then a bright red colour. It finally becomes dark red, and a yellowish-green residue separates with evolution of nitrogen and hydrogen cyanide. When submitted to steam distillation, the product yields a dark oil, which crystallises to a red mass, melting at about 45°. When concentrated sulphuric acid is added, the product becomes bright green and then brown. A. McK.

1:3-Dimethylcyclohexane derived from Camphoric Acid. LUIGI BALBIANO and L. ANGELONI (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 142—148).—The reduction of camphoric acid by means of phosphorus and hydriodic acid yields 1:3-dimethylcyclohexane (Zelinsky, *Abstr.*, 1895, i, 411), which, on oxidation with nitric acid, gives trinitro-*m*-xylene and formic and glutaric acids. The reduction of the camphoric acid takes place according to the following scheme:



Preparation of Benzene and its Homologues from Russian Naphtha by Nikiforoff's Method. W. N. OGLOBLIN (*Zeit. Farb. Text. Ind.*, 1904, 3, 293—294. Compare this vol., i, 729).—The naphtha is first passed, under the ordinary pressure, through retorts heated at 525—550°, and the distillate obtained heated at 1200° under a pressure of two atmospheres. Every 100 grams of the naphtha gives, under this treatment, 38.9 grams of "grey benzene," which

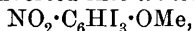
consists of a mixture of 5.59 grams of benzene, 4.00 of toluene, and 2.11 of xylene; after fractionation, 4.56 grams of pure benzene are obtained. The fact that the product contains neither acids nor bases renders its purification easy, and makes this method of preparation of benzene and its homologues preferable to that involving the distillation of coal-tar.

W. A. D.

Ozobenzene. CARL D. HARRIES and VALENTIN WEISS (*Ber.*, 1904, 37, 3431—3433. Compare Renard, *Abstr.*, 1895, i, 593; this vol., i, 361).—Ozobenzene, $C_6H_6O_3$, is formed as an opalescent, gelatinous mass when a current of ozone is passed through benzene for 1—2 hours at 5—10°. Commercial benzene, which is free from thiophen and has been distilled over sodium, forms ozobenzene. On evaporation of the excess of benzene, the product is obtained as a white, amorphous, highly explosive mass, which, on treatment with water at 0°, is converted into an even more explosive crystalline modification. Not more than 0.1 gram of ozobenzene should be prepared at one time. Under reduced pressure, or in a current of air, it gradually volatilises; it is sparingly soluble, or insoluble, in the ordinary solvents. When carefully warmed with water, ozobenzene yields glyoxal, which is identified by conversion into its osazone. Ozobenzene, or benzenetri-

ozonide, is represented by the formula $O_3 \begin{array}{c} \diagup \quad \diagdown \\ \text{CH} \cdot \text{CH} \cdot \text{CH} \\ \diagdown \quad \diagup \\ \text{CH} \cdot \text{CH} \cdot \text{CH} \\ \diagup \quad \diagdown \\ O_3 \end{array}$. G. Y.

Certain Derivatives of 1:3:5-Tri-iodo-2:4-dinitrobenzene. C. LORING JACKSON and J. F. LANGMAID (*Amer. Chem. J.*, 1904, 32, 297—308).—When 1:3:5-tri-iodo-2:4-dinitrobenzene is boiled with sodium methoxide, it is converted into *tri-iodonitroanisole*,



which crystallises from alcohol in white or very pale yellow, slender prisms, melts at 128°, and is soluble in benzene, ether, chloroform, acetone, carbon disulphide, or acetic acid; a small quantity of a crystalline substance [possibly $NO_2 \cdot C_6HI(OMe)_3$], which melts at 253—256°, is also produced in this reaction.

By the action of sodium ethoxide on tri-iododinitrobenzene, a compound is obtained which melts at 130° and is probably identical with the dinitroresorcinol diethyl ether described by Jackson and Warren (*Abstr.*, 1891, 1025); a small quantity of another substance is produced which crystallises in plates and melts at about 200°.

When tri-iododinitrobenzene is treated with ethyl sodiomalonate, di-iododinitrobenzene, ethyl iododinitrophenylmalonate, an additive compound of di-iododinitrobenzene and tri-iododinitrobenzene, and a substance which melts at 73° and does not contain iodine are obtained. The di-iododinitrobenzene melts at 160° and is probably identical with the compound prepared by Istrati and Georgescu (*Abstr.*, 1892, 1310) by the action of nitric acid on tri-iodobenzene. *Ethyl iododinitrophenylmalonate*, $C_6H_2I(NO_2)_2 \cdot CH(CO_2Et)_2$, crystallises from alcohol in

yellow, rhombic plates, melts at 83° , and is soluble in ether, benzene, chloroform, acetone, glacial acetic acid, or carbon disulphide. The additive compound, $2\text{C}_6\text{H}_2\text{I}_2(\text{NO}_2)_2 \cdot \text{C}_6\text{I}_3(\text{NO}_2)_3$, crystallises from alcohol in pale yellow, long, slender prisms, melts at 182° , and is soluble in benzene, ether, chloroform, acetone, or carbon disulphide. E. G.

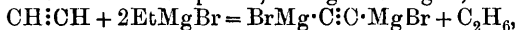
Action of Magnesium Ethyl Iodide on Nitrobenzene. BERNARDO ODDO (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 220—224). The action of magnesium ethyl iodide on nitrobenzene in ethereal solution yields a compound, $\text{O:NPhEt} \cdot \text{O} \cdot \text{MgI}$, which with pyridine gives an additive compound, $\text{C}_8\text{H}_{10}\text{O}_2\text{IMg} \cdot \text{C}_5\text{H}_5\text{N}$. The action of water on the first compound yields ethylaniline as the principal product.

T. H. P.

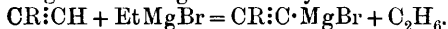
A. Chloro-1:8-dihydroxynaphthalene-3:6-disulphonic Acid. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 153195).—A chloro-1:8-dihydroxynaphthalene-3:6-disulphonic acid, prepared by the action of alkaline hypochlorite solutions on 1:8-dihydroxynaphthalene-3:6-disulphonic acid (chromotropic acid), separates from dilute sodium chloride solution in colourless crystals and combines readily with diazonium salts.

C. H. D.

Action of Acetylene on Magnesium Phenyl Bromide. BERNARDO ODDO (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 187—193).—It has been shown by Jocitsch (*Bull. Soc. chim.*, 1902, [iii], 28, 208) that on passing acetylene into an ethereal solution of magnesium methyl-bromide, ethane and the compound, $\text{BrMg} \cdot \text{C} \equiv \text{C} \cdot \text{MgBr}$, are formed :



whilst with the higher homologues of acetylene the action is :



The magnesio-acetylene derivatives thus obtained resemble, in their behaviour, the compounds prepared by Grignard (*Abstr.*, 1901, i, 263) ; thus, with water they yield the corresponding acetylenic hydrocarbon, with ketones they give tertiary acetylenic alcohols, and with aldehydes secondary acetylenic alcohols. All these compounds have the $\cdot \text{C} \equiv \text{C} \cdot$ group arranged between two carbon atoms. The compounds prepared by the author are described below.

Magnesio-acetylene bromide, $\text{HC} \equiv \text{C} \cdot \text{MgBr}$, prepared by passing acetylene into the ethereal solution obtained by the action of powdered magnesium and iodine on an ethereal solution of bromobenzene, forms an oily liquid, which undergoes change in moist air and gives a vigorous evolution of acetylene when treated with water. With pyridine in ethereal solution, it yields the compound $\text{HC} \equiv \text{C} \cdot \text{MgBr} \cdot \text{C}_5\text{H}_5\text{N} \cdot \text{Et}_2\text{O}$ as a yellow precipitate. With benzaldehyde, it gives : (1) a hydrocarbon, $\text{C}_{18}\text{H}_{14}$, which separates from light petroleum in white, nacreous crystals melting at 213 — 214° , and soluble in benzene, chloroform, or carbon disulphide and to a slight extent in alcohol, ether, or light petroleum ; it dissolves in boiling nitric acid, which, on cooling, deposits needles which do not melt at 270° . (2) The ether of phenylacetylenecarbinol, $\text{CH} \equiv \text{C} \cdot \text{CHPh} \cdot \text{O} \cdot \text{CHPh} \cdot \text{C} \equiv \text{CH}$, which boils at 155 — 160° under 10 mm. pressure. (3) A liquid boiling at 196 — 200° and having a composition

agreeing well with the formula $C_{18}H_{14}O$. The two latter compounds are being further investigated. T. H. P.

Electrolytic Oxidation of Anthracene. A. FONTANA and FREDERICK M. PERKIN (*Chem. Centr.*, 1904, ii, 708—709; from *Elektrochem. Zeit.*, 11, 99—105).—One hundred grams of acetone dissolve 1.053 of anthracene at 21° and 1.664 at 36° , whilst the solubility of anthraquinone is 0.536 at 20° and 0.812 at 36° . For the purpose of electrolytic oxidation, 10 grams of anthracene are dissolved in a mixture of 550 c.c. of acetone and 100 c.c. of a 40 per cent. solution of sulphuric acid. The solution becomes clear on warming, but the presence of undissolved anthracene is not disadvantageous since, as the quinone is formed, more anthracene is dissolved. The oxidation was effected at about 40° in a glass cell with platinum electrodes, using a current density of 1—3 amperes per sq. dcm. The anode rotated between two cathodes which were contained in porous cells. When a leaden vessel is used for the anode compartment, the product has a dark colour. A yield of 55 per cent. was obtained; in alkaline solution, the yield is less. Yields of up to 80 per cent. may be obtained by adding oxygen carriers, without using special solvents, but employing the anthracene in fine suspension. Experiments with chromium compounds (chromate or chrome alum), manganese in acid or alkaline solutions (manganese sulphate or potassium permanganate), and cerium sulphate are described in the original paper. In most cases, the product consisted of dark yellow crystals, but pale yellow crystals were obtained when an acid solution of a manganese salt was added. By using a comparatively small cathode surface and a large anode, the same results may be practically obtained without employing a diaphragm, but the process is somewhat slower. E. W. W.

Researches in the Phenanthrene Series. ALFRED WERNER (*Ber.*, 1904, 37, 3083—3088).—A reply to certain criticisms by Schmidt (this vol., i, 69—71) of the author's earlier work.

W. A. D.

β -Dibromophenanthrene. ALFRED WERNER and A. EGGER (*Ber.*, 1904, 37, 3026—3030. Compare *Abstr.*, 1902, i, 437).—The action of bromine on phenanthrene in carbon disulphide solution leads to the formation of a dibromophenanthrene, $C_{14}H_8Br_2$, which crystallises in long, white needles, melts at 146° , and is probably identical with Zetter's α -dibromophenanthrene (*Abstr.*, 1878, 510). Zetter's supposed β -dibromophenanthrene (*loc. cit.*), obtained by bromination of phenanthrene in ethereal solution, is identical with Fittig and Schmitz's dibromofluorene (*Annalen*, 1878, 193, 137), which crystallises from ether in leaflets, from benzene in triclinic plates, melts at 164° , and is oxidised by chromic acid in glacial acetic acid solution to Holm's β -dibromofluorenone (*Abstr.*, 1883, 921), which melts at 202° .

G. Y.

Derivatives of Triphenylmethane. EMIL FISCHER and OTTO FISCHER (*Ber.*, 1904, 37, 3355—3360).—The authors found (*Annalen*,

1878, 194, 242) that when trinitrotriphenylmethane in glacial acetic acid solution is oxidised by chromic acid, the melting point of the carbinol formed is 171—172°. O. Fischer and G. Schmidt (*Zeit. Farb. Text. Ind.*, 3, 1) have since found that when the oxidation is conducted in alkaline solution with oxygen, the carbinol formed melts at 188—189°, this being identical with the figure obtained by Gomberg (this vol., i, 490), who oxidised trinitrotriphenylmethane at 100° with chromic acid. The cause of this variation in the melting point of trinitrotriphenylcarbinol has now been studied.

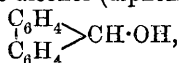
When the product obtained by the oxidation with chromic acid is repeatedly crystallised from benzene or glacial acetic acid, the carbinol melting at 188—189° is obtained. With one crystallisation of the crude product, however, the melting point varies between 165° and 170°. Trinitrotriphenylcarbinol exhibits dimorphism. The one form, melting at 189°, is monoclinic. The other form is obtained by oxidising trinitrotriphenylmethane by air at 0°; the benzene layer remaining after shaking out the alcohol with water is then quickly evaporated, the residue dissolved in cold ethyl acetate, and the crystallisation accelerated by the addition of light petroleum. When the solution is allowed to crystallise slowly, iridescent crystals of the rhombic form, melting at 167°, separate. These crystals lose their lustre after several days; they do not, however, lose weight in so doing, but the melting point rises from 4° to 5°. The rhombic form, accordingly, is the unstable variety, which is gradually transformed into the stable monoclinic form.

The crude hydrocarbon, obtained by the oxidation of leucaniline, was mixed with a trace of diphenyl-*m*-tolylmethane (compare Bistrzycki and Gyr, this vol., i, 315). The crystals which separated melted at 60—61°, and when oxidised yielded the carbinol, melting at 68—69°; the mother liquor from which the crystals had been removed yielded a product melting at 62—67°, which, when oxidised, formed the carbinol melting at 150°.

In the transformation of leucaniline into diphenyltolylmethane, an excess of strong sulphuric acid and of nitrous fumes should be avoided by decomposing the diazo-compound slowly.

When diphenyl-*m*-tolylmethane (m. p. 61—62°) is oxidised by chromic acid, the corresponding carbinol and an oil, which is probably phenyl-*m*-tolyl ketone, are formed. A. McK.

9:10-Diphenylphenanthrene, a Product of Intramolecular Rearrangement. ALFRED WERNER and ARMIN GROB (*Ber.*, 1904, 37, 2887—2903).—Fluorene alcohol (diphenylcarbinol),



is best prepared by reducing fluorenone (diphenylene ketone) with zinc dust. Phosphorus pentachloride converts it into *diphenylenechloro-*

methane, $\begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{array} > \text{CHCl}$, crystallising from alcohol in long, colourless needles and melting at 90°. The chloro-compound reacts with benzene and aluminium chloride, and after decomposing with water and

distilling the benzene layer, phenylfluorene (phenyldiphenylene-methane), $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{CHPh}$, is obtained, melting at 146—148° (compare Hanriot and St. Pierre, Abstr., 1889, 882). Phenylfluorene dissolves potassium at 240—280°, and the product reacts with benzoyl chloride on boiling, forming benzoylphenylfluorene, $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{CHPh} \cdot \text{COPh}$, which is identical with the compound obtained from triphenylmethane by Hanriot and St. Pierre. Distillation with zinc dust or heating with alcoholic potassium hydroxide at 200° regenerates the phenylfluorene. Hydriodic acid and red phosphorus under pressure reduce the benzoyl compound to diphenylphenanthrene.

o-Dibenzoyldiphenyl, $\text{COPh} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{COPh}$, prepared by heating *o*-bromobenzophenone with copper powder at 260—360°, crystallises in prisms and melts at 165—167° (compare Klinger and Lonnes, Abstr., 1896, i, 691). When distilled with zinc dust, 9:10-diphenylphenanthrene, $\begin{smallmatrix} \text{C}_6\text{H}_4 \cdot \text{CPh} \\ | \\ \text{C}_6\text{H}_4 \cdot \text{CPh} \end{smallmatrix}$, is obtained, crystallising in colourless needles and melting at 233—234°. Chromic acid oxidises it again to the dibenzoyl compound.

Zinc and potassium hydroxide reduce *o*-dibenzoyldiphenyl to a pinacone, $\text{C}_{26}\text{H}_{20}\text{O}_2$, crystallising from alcohol in small, white needles and melting at 202—204°. Hydriodic acid and red phosphorus reduce it to 9:10-diphenylphenanthrene.

Phenanthraquinone and magnesium phenyl iodide react to form a pinacone, dihydroxydiphenyldihydrophenanthrene, $\begin{smallmatrix} \text{C}_6\text{H}_4 \cdot \text{CPh} \cdot \text{OH} \\ | \\ \text{C}_6\text{H}_4 \cdot \text{CPh} \cdot \text{OH} \end{smallmatrix}$, separating from water in colourless crystals and melting at 178—179°. This compound appears to be stereoisomeric with the above-named pinacone. It yields 9:10-diphenylphenanthrene on distillation with zinc dust. Both pinacones yield *o*-dibenzoyldiphenyl on oxidation with chromic acid, and form the same anhydride, $\text{C}_{26}\text{H}_{18}\text{O}$, on heating with hydrochloric and sulphuric acids at 200—220°. The anhydride crystallises from alcohol in rhombic prisms and melts at 194—196°. It yields 9:10-diphenylphenanthrene on distillation with zinc dust.

C. H. D.

The Anthracene Series. Dibenzylanthracene and its Derivatives. EDUARD LIPPMANN and RODOLFO FRITSCH (*Monatsh.*, 1904, 25, 793—807. Compare Abstr., 1902, i, 754).—When pure, bromodibenzylanthracene melts, if rapidly heated, at 187°, without decomposing.

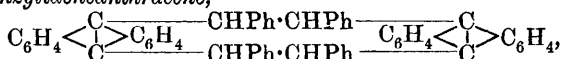
Dibenzylideneanthracene, $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{C} \\ | \\ \text{C} \end{smallmatrix} > \text{C}_6\text{H}_4 \begin{smallmatrix} \text{CHPh} \\ | \\ \text{CHPh} \end{smallmatrix}$, is prepared by

heating bromodibenzylanthracene with acetic anhydride; it is also formed when the bromine compound is heated at 125—130°, or boiled with dilute potassium carbonate solution, or heated with glacial acetic acid, or with a benzene solution of quinoline (2 mols.). It is precipitated, on addition of alcohol to its solution in chloroform, in yellow crystals

and melts at 234—236° (some preparations melted at 237—240°). The action of bromine on dibenzylideneanthracene in chloroform solution leads to the evolution of hydrogen bromide and the formation of a residue containing bromine; when boiled with xylene, the residue loses bromine and yields a *product* which melts at 243°; if boiled with glacial acetic acid, the residue forms a *substance* which is free from bromine, melts at 199°, and yields potassium acetate when hydrolysed with potassium hydroxide.

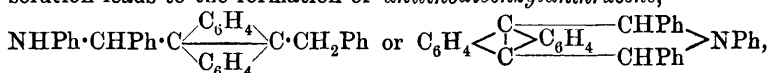
If bromodibenzylanthracene is boiled with aqueous potassium or lead acetate, the product is a mixture of dibenzylideneanthracene and bisdibenzylideneanthracene, which is the main product if the bromine compound is boiled with 1 mol. of quinoline in benzene solution for ten hours before the addition of a second molecular proportion of quinoline.

Bisdibenzylideneanthracene,



forms compact, yellow crystals, melts at 184°, dissolves in chloroform to a red, fluorescent solution, and gives a green coloration with concentrated sulphuric acid.

The action of aniline on bromodibenzylanthracene in chloroform solution leads to the formation of *anilinodibenzylanthracene*,



which is obtained in yellowish-green crystals and melts at 233°. The ethoxy-derivative, obtained by the action of alcohol on the bromine compound in boiling benzene solution, forms crystals containing 1 mol. of benzene, which melt at 217°, lose C₆H₆ at 178°, and then melt at 197°. When boiled with dilute sulphuric acid, the ethoxy-derivative yields the *ether*, C₂₈H₂₁·O·C₂₈H₂₁, which crystallises in white scales and melts at 213—215°. *Acetoxydibenzylanthracene*, formed by the action of silver acetate on the bromine compound in chloroform solution, melts at 158° and is hydrolysed by alcoholic potassium hydroxide to *hydroxydibenzylanthracene*, CH₂Ph·C₁₄H₈·CHPh·OH, which forms flesh-coloured crystals and melts at 151°. G. Y.

Glycerol Derivatives of Aromatic Bases. PAUL COHN and PAUL FRIEDLÄNDER (*Ber.*, 1904, 37, 3034—3036).—*p*-Toluidine combines with epichlorohydrin to form a compound, C₁₀H₁₄ONCl, crystallising in colourless needles from benzene and melting at 81—82°. When heated with sodium ethoxide, this is converted into the compound C₇H₇·NH·CH₂·CH(OH)·CH₂·OEt, forming colourless needles and melting at 41—42°. On heating with 2 molecules of toluidine, epichlorohydrin forms the compound C₁₇H₂₂ON₂, melting at 113.5°. This gives a *dinitrosoamine* crystallising in yellowish-white needles melting at 223°; the corresponding *nitrosoamine* of the mono-toluidine product melts at 70.5°. E. F. A.

Spatial Configuration of Tervalent Nitrogen Compounds. HUMPHREY O. JONES and J. P. MILLINGTON (*Proc. Camb. Phil. Soc.*, 1904, 12, [vi], 489—492).—The authors have made experiments on

the resolution of nitrogen compounds of the type $\text{NR}^{\text{I}}\text{R}^{\text{II}}\text{R}^{\text{III}}$ by methods which would not involve a change in the active valency of the nitrogen atom (compare Kipping and Salway, *Trans.*, 1904, 85, 438).

α -Phenylbenzylhydrazine gave a *d*-camphorsulphonate forming prisms melting at 156—157°, and having $[\text{M}]_{\text{D}}$ in 2 per cent. solution +53—54°. No resolution of the base was obtained.

Methylethylaniline, on sulphonation, yields *methylethylanilinesulphonic acid* melting at 249—250°, easily soluble in water, less readily in alcohol, and forming a *barium* salt crystallising with $2\text{H}_2\text{O}$. The *brucine* salt, $\text{C}_{32}\text{H}_{39}\text{O}_7\text{N}_3\text{S}_4\text{H}_2\text{O}$, forms lustrous prisms soluble to the extent of about 1 per cent. in water, and sparingly soluble in organic solvents. After dehydration, it melts at about 90°. It gives $[\text{M}]_{\text{D}} -120^\circ$, no alteration, indicating a resolution, being obtained on fractional crystallisation.

G. D. L.

Preparation of Salts of Dialkylaminomethanesulphonic Acids. EMIL KNOEVENAGEL (*D.R.-P.* 153193).—The alkali hydrogen sulphite compounds of formaldehyde (hydroxymethanesulphonates) react with secondary amines forming dialkylaminomethanesulphonates. Thus formaldehyde, sodium hydrogen sulphite, and methylaniline combine on warming to form *sodium phenylmethylanilaminomethanesulphonate*, $\text{NPhMe}\cdot\text{CH}_2\cdot\text{SO}_3\text{Na}$. Ethylaniline, benzylaniline, diethylamine, and piperidine react in similar manner. The sulphonates crystallise from water or dilute alcohol and are hydrolysed by heating with alkalis. Metallic cyanides convert them into dialkylaminoacetoneitriles.

C. H. D.

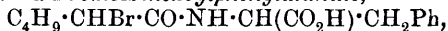
N- α -Naphthylhydroxylamine. JOHANNES SCHEIBER (*Ber.*, 1904, 37, 3055—3057).—In contradistinction to Wacker's observations (*Abstr.*, 1901, i, 655), naphthylhydroxylamine melts at 78—79°, crystallises in faintly yellow, glistening plates, and has the composition $\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}$.

E. F. A.

Hydrolysis of Dipeptides with Pancreas Ferment. EMIL FISCHER and PETER BERGELL (*Ber.*, 1904, 37, 3103—3108. Compare *Abstr.*, 1903, i, 694).—Under the influence of trypsin glycyl-*l*-tyrosine is converted into *l*-tyrosine and glycine, about 50—55 per cent. of the theoretical quantity of tyrosine crystallising from solution. The racemic form of *leucylalanine*, which melts and decomposes at 245°, is resolved into *leucyl-d*-alanine and an active dipeptide, probably *leucyl-l*-alanine. Similarly, *alanyl-leucine* and *leucyl-leucine* were resolved into an active dipeptide and two amino-acids. Hydrolysis is very incomplete in these three cases and the authors emphasise the importance of working with fresh pancreatic secretions.

E. F. A.

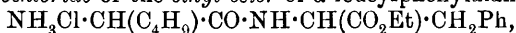
Syntheses of Polypeptides. VI. Derivatives of Phenylalanine. HERMANN LEUCHS and UMETARO SUZUKI (*Ber.*, 1904, 37, 3306—3315. Compare *Abstr.*, 1903, i, 465, 607, 799; this vol., i, 652, 771, 890).— α -*Bromoisohexoylphenylalanine*,



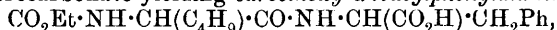
obtained by the action of α -bromohexoyl chloride on phenylalanine in the presence of alkali, crystallises from toluene in colourless, double, six-sided pyramids. It melts at $119\text{--}123^\circ$ (corr.) and is readily soluble in most organic solvents with the exception of benzene, toluene, and light petroleum. That it is a mixture of two stereoisomerides is proved by the action of ammonia at 100° , when α - and β -leucylphenylalanines, $\text{C}_4\text{H}_9\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\text{Ph}$, are obtained. The α -compound crystallises from dilute alcohol in minute prisms containing $1\text{H}_2\text{O}$, which it loses at $105\text{--}110^\circ$. It melts at $220\text{--}223^\circ$ (corr.), is readily soluble in hot water, but practically insoluble in the usual organic solvents. Its aqueous solution has an acid reaction and it dissolves in both alkalis and acids. Its faintly acidified solution gives a copious precipitate with phosphotungstic acid, but this dissolves either on warming or in the presence of a large excess of mineral acid. Its phenylcarbimide derivative,

$\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{C}_4\text{H}_9)\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\text{Ph}$, crystallises in six-sided, rhombic plates, melts and decomposes at $193\text{--}195^\circ$ (corr.), and dissolves fairly readily in alcohol, ether, ethyl acetate, or acetone.

The hydrochloride of the ethyl ester of α -leucylphenylalanine,



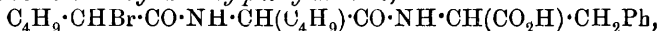
obtained by warming the α -compound for a short time with an alcoholic solution of hydrogen chloride, crystallises from hot alcohol in minute, four-sided plates, melts and decomposes at $193\text{--}195^\circ$ (corr.), and is readily soluble in water. The α -compound reacts with ethyl chlorocarbonate yielding carbethoxy- α -leucylphenylalanine,



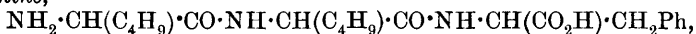
which crystallises in needles, melts at $140\text{--}141.5^\circ$ (corr.), and is readily soluble in alcohol or ether.

β -Leucylphenylalanine is insoluble in dilute alcohol, is anhydrous, and melts and decomposes when quickly heated at 259° (corr.). Its phenylcarbimide derivative crystallises in small needles and melts and decomposes at $183\text{--}184^\circ$ (corr.).

α -Bromoisohexoyl- α -leucylphenylalanine,

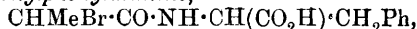


obtained by the action of α -bromoisohexoyl chloride on α -leucylphenylalanine, crystallises from benzene in colourless needles, melts at $163\text{--}165^\circ$ (corr.), and dissolves readily in chloroform. When heated with aqueous ammonia at 100° , it yields leucyl- α -leucylphenylalanine,

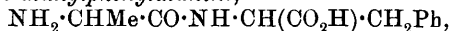


which crystallises from 80 per cent. alcohol with $2\text{H}_2\text{O}$, and melts at $225\text{--}227^\circ$ (corr.) to a colourless oil.

α -Bromopropionylphenylalanine,



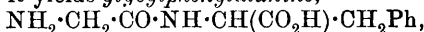
crystallises from benzene in colourless needles, melts at $132\text{--}133^\circ$ (corr.), and is readily soluble in most organic solvents. Ammonia converts it into alanylphenylalanine,



which is precipitated from its aqueous solutions, on the addition of

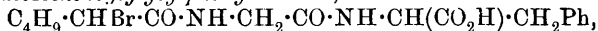
alcohol, in the form of short prisms containing $2\text{H}_2\text{O}$ and decomposing and melting at $241-243^\circ$ (corr.).

Chloroacetylphenylalanine, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\text{Ph}$, melts at $130-131^\circ$ (corr.) and crystallises from water in four-sided plates. With ammonia, it yields *glycylphenylalanine*,

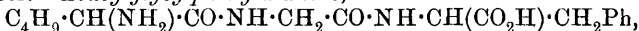


which melts and decomposes at 270° when rapidly heated.

α -Bromoisohexoylglycylphenylalanine,

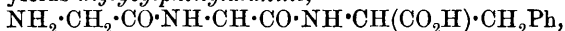


melts at $163-164^\circ$ (corr.) and is insoluble in benzene, light petroleum, or water. *Leucylglycylphenylalanine*,



melts and decomposes at $225-228^\circ$ (corr.).

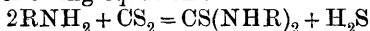
Chloroacetylglycylphenylalanine melts at $151-152^\circ$ and with ammonia yields *diglycylphenylalanine*,



which melts and decomposes at $238-239^\circ$ (corr.). It dissolves readily in hot water and crystallises in long needles. With cupric salts and alkali, it gives a bluish-violet coloration.

J. J. S.

Study and Synthetical Preparation of some *s*-Arylthiocarbamides. EMMANUEL POZZI-ESCOT (*Compt. rend.*, 1904, 139, 450-451).—The author obtains a quantitative yield of the *s*-arylthiocarbamide by heating the corresponding aromatic amine in alcoholic solution with excess of carbon disulphide in the presence of potassium hydroxide, according to the following equation :



(compare, however, Weith, *Ber.*, 1873, 6, 967). No new compounds are described.

M. A. W.

p-Tolytaurine. HANS WOLFBAUER (*Monatsh.*, 1904, 25, 682-686).—When oxidised with potassium chlorate and fuming hydrochloric acid (compare Andreasch, *Abstr.*, 1883, 664), 2-*p*-tolylimino-3-*p*-tolylidihydrothiazoline yields the *anhydride* of di-*p*-tolyltaurocarbamic acid, $\text{CO}\langle\text{N}(\text{C}_7\text{H}_7)-\text{SO}_2\rangle\text{CH}_2$, which crystallises in glistening leaflets, melts at 204° , and is insoluble in water, but moderately soluble in boiling alcohol or glacial acetic acid. When boiled with baryta in aqueous solution, the anhydride yields carbon dioxide, *p*-toluidine, and the *barium* salt of *p*-tolyltaurine, $(\text{C}_9\text{H}_{12}\text{O}_3\text{NS})_2\text{Ba}$, which crystallises in glistening leaflets.

p-Tolytaurine, $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$, crystallises in thin leaflets or plates, melts and decomposes at 254° , is easily soluble in water, alcohol, or glacial acetic acid, but only slightly so in ether, and gives a strongly acid reaction, decomposing carbonates with evolution of carbon dioxide.

G. Y.

[*Aminotolylthiocarbamide*.] FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 152027).—On adding potassium thiocyanate

to a solution of tolylene-2:4-diamine hydrochloride, the *monothiocyanate* is formed. This is converted on heating at 120° into *aminotolylthiocarbamide*, which forms a greyish-white powder, dissolving sparingly in water or alcohol, more readily in hot acids, and melting at 170° . A yellow dye is obtained on heating it with sulphur at $200-250^{\circ}$.
C. H. D.

Picramic Acid (Dinitraminophenol). A. FRÉBAULT and JULES ALOY (*J. Pharm. Chim.*, 1904, [vi], 20, 245—247).—Picramic acid is best prepared by boiling an aqueous or methyl alcoholic solution of picric acid with slight excess of ammonia and zinc powder for half an hour, the liquid being from time to time mixed with a little more ammonia. Picramic acid, unlike picric acid, is not explosive when suddenly heated. It does not precipitate peptones, albumoses, albumin, or alkaloids. With sodium hypobromite, it yields bromopicrin, $\text{CBr}_3 \cdot \text{NO}_2$.

Estimation of Potassium.—Potassium picrate, obtained in due course by precipitation with sodium picrate in the presence of alcohol, is boiled with sodium carbonate and dextrose, which reduces the picrate to picramate, which is then estimated colorimetrically.

L. DE K.

Preparation of *p*-Aminophenol-*m*-sulphonic Acid. KALLE & Co. (D.R.-P. 153123. Compare this vol., i, 664).—In the former method of preparation of *p*-nitrophenol-*m*-sulphonic acid from *p*-nitroacetylmetanilic acid, nitroresorcinol is obtained as a by-product. This is avoided by boiling the nitroacetylmetanilic acid with concentrated sodium carbonate or dilute sodium hydroxide solution in a reflux apparatus, when the hydrolysis is confined to the acetylaminogroup.
C. H. D.

The rendering Active of Oxygen. XI. Autoxidation of Thiophenol. CARL ENGLER and H. BRONIATOWSKI (*Ber.*, 1904, 37, 3274—3276).—The autoxidation of thiophenol in potassium carbonate solution, or better, in dilute ammonia, has been investigated in an apparatus similar to that used by Baur (*Zeit. anorg. Chem.*, 1897, 13, 251). The thiophenol is placed in a thin-walled bulb, which can be broken after the reading is taken. The absorption of oxygen is slow and requires some seven days for completion. The results obtained agree with the absorption of one molecule of oxygen for every four molecules of thiophenol. The reaction therefore probably proceeds in the two stages: $2\text{PhSH} + \text{O}_2 = \text{Ph}_2\text{S}_2 + \text{H}_2\text{O}_2$, $2\text{PhSH} + \text{H}_2\text{O}_2 = \text{Ph}_2\text{S}_2 + 2\text{H}_2\text{O}$. The presence of hydrogen peroxide has been proved by the aid of titaniumsulphuric acid.
J. J. S.

Trinitro-*m*-cresol. ERNST MURMANN (*Chem. Centr.*, 1904, ii, 436; from *Oesterr. Chem. Zeit.*, 7, 273).—The melting point of trinitro-*m*-cresol, which had been purified by repeatedly crystallising from water and chloroform, has been found to be 109.5° .
E. W. W.

Symmetrical Trinitroxyleneol. EDMUND KNECHT and EVA HIBBERT (*Ber.*, 1904, 37, 3477—3479).—When Knoevenagel's *s*-xyleneol is nitrated by solution in a mixture of concentrated and 20 per cent. fuming sulphuric acid and admixture with concentrated nitric acid, the *trinitro*-derivative, $\text{OH} \cdot \text{C}_6\text{Me}_2(\text{NO}_2)_3$ [$\text{Me}_2 : \text{OH} : (\text{NO}_2)_3 = 1 : 3 : 5 : 2 : 4 : 6$], is obtained. It is soluble in hot water and is best purified by means of its *potassium* salt, which is sparingly soluble in potassium chloride solution. This salt forms long, brownish-yellow crystals, and when boiled with dilute hydrochloric acid yields the free trinitroxyleneol, which crystallises from hot water in straw-yellow needles melting at 108° . It is less soluble in water than picric acid, and in the sulphuric acid bath dyes wool a somewhat redder shade than picric acid. It reacts with ammonium sulphide in the same manner as picric acid and trinitrocresol, but is not affected by potassium cyanide.

Potassium dinitroxyleneolsulphonate, $\text{OH} \cdot \text{C}_6\text{Me}_2(\text{NO}_2)_2 \cdot \text{SO}_3\text{K}$, is obtained as a by-product in the preparation of the trinitro-compound.

J. J. S.

Action of Nitrous Acid on Brominated Phenols. G. DAHMER (*Annalen*, 1904, 333, 346—370).—It has been shown by Thiele (*Abstr.*, 1900, i, 500) and Zincke (*Abstr.*, 1900, i, 545) that in the action of nitrous acid on phenols a hydrogen or bromine atom in the ortho-position is replaced by the nitro-group. This reaction has now been more fully investigated.

Of the monobromophenols, only the para-compound yields a single product, namely, 4-bromo-2-nitrophenol (m. p. $89-90^\circ$).

Both 2-bromo- and 2:6-dibromothymol ($\text{Me} : \text{Pr} : \text{OH} : \text{Br}_2 = 1 : 4 : 3 : 2 : 6$) yield with sodium nitrite in acetic acid solution 6-bromo-2-nitrothymol, melting at $109-110^\circ$. The dibromothymol, prepared by the action of bromine in chloroform solution, is a viscid, colourless liquid boiling at $187-188^\circ$ under 34 mm. pressure; the *acetyl* derivative melts at $54-55^\circ$. On attempting to brominate dibromothymol further, tetrabromo-*m*-cresol (m. p. $191-192^\circ$) is formed.

3:5-Dibromocarvacrol (3:5-dibromo-4-propyl-*o*-cresol)

($\text{Me} : \text{Pr} : \text{OH} : \text{Br}_2 = 1 : 4 : 2 : 3 : 5$)

is converted, when similarly treated, into 3:5-dinitrocarvacrol, which crystallises in needles melting at $116-117^\circ$.

s-Tribromoresorcinol [$(\text{OH})_2 : \text{Br}_3 = 1 : 3 : 2 : 4 : 6$] is converted into 2:4-dibromo-6-nitroresorcinol, which crystallises in scales melting at $148-149^\circ$. It is noteworthy that the bromine atom replaced by the nitro-group is not one of the two atoms which are in the ortho-position relative to the same hydroxyl group. On reduction with tin and hydrochloric acid, 2:4-dibromo-6-aminoresorcinol is obtained as a very easily oxidisable hydrochloride; with acetic anhydride, a *tetra-acetyl* derivative is obtained as a yellow, crystalline powder melting at $123-125^\circ$. On treatment with nitric acid in acetic acid solution, 2-bromo-4:6-dinitroresorcinol is produced, two bromine atoms being eliminated, the one which occupies the position between the two hydroxyl groups remaining.

The effect of the presence of an aldehyde or carboxyl group was

investigated, using 3:5-dibromo-*p*-hydroxybenzaldehyde and 3:5-dibromosalicylic acid as examples. Nitrous acid attacks the hydroxy-aldehyde but slowly, bromonitrohydroxybenzoic acid being probably produced. In the case of the salicylic acid, the reaction only begins at a high temperature, when the nitro-group replaces the carboxyl group, 2:4 dibromo-6-nitrophenol being formed. Nitric acid acts in a similar manner.

Although dibromodiphenol is attacked by nitric acid in acetone solution, no product could be isolated. Diphenylmethane derivatives, on the other hand, reacted easily with nitrous acid. In tetrabromodihydroxydiphenylmethane [$\text{CH}_2:\text{OH}:\text{Br}_2=1:4:3:5$], a bromine atom is replaced in each nucleus, *dibromodinitrodihydroxydiphenylmethane* [$\text{CH}_2:\text{OH}:\text{Br}:\text{NO}_2=1:4:3:5$] being formed and crystallising in golden-yellow needles melting at 232° ; the *diacetyl* derivative melts at 185° . *Hexabromodihydroxydiphenylmethane* [$\text{CH}_2:\text{OH}:\text{Br}_3=1:4:2:3:5$]

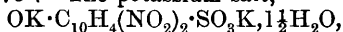
yields *tetrabromodinitrodiphenylmethane* [either $\text{CH}_2:\text{OH}:\text{Br}_2:\text{NO}_2=1:4:2:3:5$ or $1:4:2:5:3$], which crystallises in dark yellow prisms melting at 244° ; the *diacetyl* derivative melts at 167° .

When treated with nitrous acid, 2:4-dibromo- α -naphthol yields a blue compound and 4-bromo-2-nitro- α -naphthol. 1:6-Dibromo- β -naphthol behaves quite normally, yielding 6-bromo-1-nitro- β -naphthol, which Armstrong and Rossiter (Proc., 1891, 7, 87) obtained by the action of nitric acid on the dibromonaphthol. The *acetyl* derivative forms pale yellow needles melting at $115\text{--}117^\circ$. K. J. P. O.

Synthesis of Estragol and of Aromatic Derivatives containing an Unsaturated Chain. MARC TIFFENEAU (*Compt. rend.*, 1904, 139, 481—482. Compare Abstr., 1903, i, 241; Werner and Zilkens, Abstr., 1903, i, 615; Houben, Abstr., 1903, i, 805).—Phenylpropylene, $\text{CHPh}:\text{CHMe}$, is obtained by the action of β -bromostyrene on magnesium methyl iodide at a temperature of about 100° . Methylstilbene, $\text{CPhMe}:\text{CHPh}$, is similarly prepared from magnesium phenyl bromide and $\text{MgBr}\cdot\text{O}\cdot\text{CPhMe}\cdot\text{CH}_2\text{Cl}$ at $120\text{--}130^\circ$.

Allylbenzene, obtained by the action of allyl bromide on magnesium phenyl bromide in the cold, boils at $156\text{--}157^\circ$, has a sp. gr. 0.9012 at 15° and n_D 1.3143. Estragol synthesised from allyl bromide and the organomagnesium derivative of *p*-bromoanisole boils at $215\text{--}216^\circ$, has a sp. gr. 0.9755 at 15° , n_D 1.5236, and is converted by the action of alcoholic potash into anethole. M. A. W.

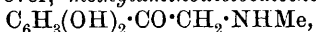
Naphthol-Yellow S. EDMUND KNECHT and EVA HIBBERT (*Ber.*, 1904, 37, 3475—3477. Compare Lauterbach, Abstr., 1882, 63).—Dinitro- α -naphtholsulphonic acid has been prepared and purified by Lauterbach's method; it crystallises in pale yellow needles containing $3\text{H}_2\text{O}$, and dissolves readily in water or alcohol. When anhydrous, it melts to a clear yellow liquid between 140° and 150° , which slowly decomposes below 175° . The potassium salt,



forms long, thin, elastic crystals of an orange-yellow colour. This salt, like all the others, turns red on warming and yellow again on

cooling, and explodes when strongly heated. The *sodium* salt contains $3\text{H}_2\text{O}$, the *ammonium* salt is anhydrous, and the *calcium* salt contains $4\text{H}_2\text{O}$. *Magnesium*, *silver*, *aniline*, and *p-nitraniline* salts have also been prepared. J. J. S.

Alkylamino-*o*-dihydroxyacetophenones (Alkylaminoacetocatechols). FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 152814).—Chloroacetocatechol, $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$, reacts with dimethylamine to form dimethylaminoacetocatechol, methylamine forming only a salt of the hydroxyketone (Dzierzowski, Abstr., 1894, i, 234). When the chloro-compound is gently warmed with an excess of methylamine, however, *methylaminoacetocatechol*,



is produced, and is precipitated by ammonia from acid solutions as a white, crystalline powder, darkening at 200° and decomposing at about 230° . The *hydrochloride* crystallises from alcohol in colourless leaflets and decomposes at 240° . Ferric chloride gives an emerald-green coloration.

Ethylaminoacetocatechol, prepared in similar manner, forms microscopic crystals, the *hydrochloride* forms slender needles, and decomposes at 260° .

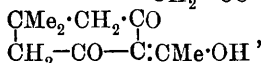
Ethanolaminoacetocatechol, from chloroacetocatechol and ethanolamine, is soluble in water, its *hydrochloride* crystallises from alcohol in leaflets, and melts at 197° . C. H. D.

Interaction of 1:3-Dicarbonyl Compounds and the Acetyl Derivatives of Dimethyl- and Phenyl-dihydroresorcinols. WALTER DIECKMANN and RICHARD STEIN (*Ber.*, 1904, 37, 3370—3384. Compare Abstr., 1900, i, 482).—The action of acetic anhydride on 1:3-dicarbonyl compounds in presence of sodium acetate leads to the formation of the *C*-acetyl derivative; ethyl acetylmalonate, formed by this method, decomposes into ethyl acetoacetate, which is further acetylated. When acted on by acetic anhydride in absence of an alkaline acetate, dimethyl- and phenyl-dihydroresorcinols yield *O*-acetyl derivatives; ethyl acetoacetate and ethyl malonate do not react with acetic anhydride alone. Von Pechmann's formation of ethyl diacetoacetate by the action of acetic anhydride on ethyl acetoacetate (Abstr., 1894, i, 274) was probably due to the alkalinity of the glass boiling vessel, as the presence of traces of an alkali acetate are sufficient to bring about the reaction on prolonged boiling. This may be avoided by the addition of a small quantity of acetyl chloride.

The *O*-acetyl derivatives of 1:3-carbonyl compounds are converted into the corresponding *C*-derivatives when heated with anhydrous sodium acetate or with acetic anhydride and sodium acetate. When boiled with acetic anhydride and pyridine, quinoline, or dimethylaniline, ethyl acetoacetate yields the *O*-acetyl derivative; with acetic anhydride and concentrated sulphuric acid, it yields a mixture of the *O*- and the *C*-acetyl derivatives. With acetic anhydride and quinoline, dimethylaniline, or pyridine at the ordinary temperature, dimethyl- and phenyl-dihydroresorcinols yield the *O*-acetyl derivative, but the *C*-derivative when boiled with acetic anhydride and pyridine.

O-Acetyldimethyldihydroresorcinol, $\begin{array}{c} \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{C} \cdot \text{OAc} \\ | \\ \text{CH} : \text{C}(\text{OH}) \cdot \text{CH} \end{array}$, is a colourless, viscid oil, boils at 144° under 18 mm. pressure, has a neutral reaction, can be titrated with phenolphthalein as indicator, is hydrolysed slowly by water and rapidly by alkali hydroxides, with formation of acetic acid and dimethyldihydroresorcinol.

C-Acetyldimethyldihydroresorcinol, $\begin{array}{c} \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{C} \cdot \text{OH} \\ | \\ \text{CH}_2 - \text{CO} - \text{CAc} \end{array}$, or



crystallises in colourless needles, melts at 36°, boils at 127—128° under 14 mm., or at 250° under the ordinary pressure, and is soluble in all organic solvents, but only slightly so in water. It has a strongly acid reaction, is only partially precipitated from its solution in an aqueous alkali hydroxide on saturation with carbon dioxide, forms an ammonium salt as a momentary precipitate on addition of anhydrous ammonia to its ethereal solution, and is hydrolysed by boiling dilute sulphuric acid, but not by aqueous alkali hydroxides or baryta. With ferric chloride in alcoholic solution, it gives an intense yellowish-red coloration; the copper salt, $(\text{C}_{10}\text{H}_{13}\text{O}_3)_2\text{Cu}$, is blue, crystallises from alcohol, and melts at about 260°. The *anilide*, $\text{C}_{16}\text{H}_{19}\text{O}_2\text{N}$, crystallises in yellow needles and melts at 129—130°; the *phenylhydrazone* of the

phenylpyrazole derivative, $\begin{array}{c} \text{CH}_2 \cdot \text{C}(\text{N} \cdot \text{NHPh}) \cdot \text{CH} \cdot \text{CMe} \\ | \qquad \qquad \qquad | \\ \text{CMe}_2 \cdot \text{CH}_2 \qquad \qquad \text{C} \cdot \text{NPh} \end{array} \text{>N}$, forms colourless needles, melts at 190°, dissolves in concentrated sulphuric acid to a blue solution, and gives Knorr's pyrazoline reaction after reduction with sodium and alcohol.

O-Acetylphenyldihydroresorcinol is a neutral, viscid oil, distils with partial decomposition at 200° under 14 mm. pressure, and is converted into the *C*-derivative when boiled with acetic anhydride and sodium acetate, pyridine, or tripropylamine.

C-Acetylphenyldihydroresorcinol, $\begin{array}{c} \text{CHPh} \cdot \text{CH}_2 \cdot \text{CO} \\ | \\ \text{CH}_2 - \text{CO} - \text{CHAc} \end{array}$, crystallises in

long, colourless needles, melts at 104°, yields an unstable *bromine* derivative, and is oxidised by sodium hypobromite or hydrogen peroxide in aqueous sodium carbonate solution to β -phenylglutaric acid. The *alkali* salts are colourless, crystalline powders; the *copper* salt, $(\text{C}_{14}\text{H}_{13}\text{O}_3)_2\text{Cu}$, is a grey, insoluble, crystalline powder; the *anilide* forms colourless needles and melts at 124—125°; the *phenylhydrazone* of the *phenylpyrazole* derivative, $\text{C}_{26}\text{H}_{24}\text{N}_4$, crystallises in colourless needles, melts at 176—178°, dissolves in concentrated sulphuric acid to a dark green solution, and, after reduction with sodium and alcohol, gives a faint pyrazoline reaction.

Schwerin's acetyl- α -diketohydrindene (Abstr., 1894, i, 194) closely resembles the *C*-acetyl derivatives of the dihydroresorcinol; it can be titrated with phenolphthalein as indicator, is not attacked by boiling aqueous alkali hydroxides, gives an intense yellowish-red coloration with ferric chloride, and forms a green *copper* salt, $(\text{C}_{11}\text{H}_7\text{O}_3)_2\text{Cu}$. It is a slightly stronger acid than the dihydroresorcinol compounds, and

is not, or only slightly, precipitated from its solution in aqueous alkali hydroxides on addition of carbon dioxide. G. Y.

Condensation of Aldehydes with *p*-Diketohexamethylene.

ROBERT STOLLÉ and W. MÖRING (*Ber.*, 1904, 37, 3486—3488).—Benzaldehyde condenses with *p*-diketohexamethylene in the presence of hydrogen chloride, forming 2-benzylquinol, $C_6H_3(OH)_2 \cdot CH_2Ph$, which crystallises from hot water in slightly coloured, glistening leaflets, melts at 105° , and boils at 230° under 13 mm. pressure. It dissolves readily in alcohol, ether, or alkalis, and reduces silver nitrate in the cold, or Fehling's solution on warming. Chromic acid oxidises it to 2-benzylquinone, $C_6H_3O_2 \cdot CH_2Ph$, crystallising in flat, yellowish-brown needles, melting at 43° , and dissolving readily in alcohol or ether.

2-Anisylquinol, $C_{14}H_{14}O_3$, prepared in similar manner from anisaldehyde and *p*-diketohexamethylene, melts at 126° and boils at 271° under 16 mm. pressure; the dibenzoyl derivative, $C_{28}H_{22}O_5$, forms a white powder and melts at 125° . 2-Anisylquinone, $C_{14}H_{12}O_3$, forms glistening, orange leaflets and melts at 43° .

In the preparation of *p*-diketohexamethylene from ethyl succino-succinate, a condensation product is obtained with the formula $C_{12}H_{14}O_3$, crystallising from alcohol in needles and melting at 133° .

C. H. D.

Picrates of Unsaturated Compounds. GIUSEPPE BRUNI and E. TORNANI (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 184—187).—The authors have experimented with the following pairs of compounds, the first members of which contain an allyl group ($\cdot CH_2 \cdot CH : CH_2$) which is replaced in the isomerides by a propenyl group ($\cdot CH : CHMe$): methyleugenol and isomethyleugenol; safrole and isosafrole; ordinary apiole and isoapiole; apiole and isoapiole from dill oil; asarone; they find that those compounds containing allyl groups in the side-chain do not yield picrates, but that those with propenyl groups readily yield picrates, as may be seen by the red or reddish-brown coloration formed on mixing their solutions with solutions of picric acid. The formation of a picrate may hence be used as a test for the presence of an allyl or propenyl group in the side-chain of an aromatic compound.

isoMethyleugenol picrate, $C_{17}H_{17}O_9N_3$, crystallises from alcohol in reddish-brown needles which decompose rapidly and melt at 40 — 45° .

Asarone picrate, $C_{18}H_{19}O_{10}N_3$, forms very dark brown needles melting at 81 — 82° .

isoSafrole picrate, $C_{16}H_{13}O_9N_3$, crystallises from alcohol in stable, bright red needles melting at 73° .

Picrate of ordinary isoapiole, $C_{18}H_{17}O_{11}N_3$, separates from alcohol in minute, reddish-brown needles which melt at 89 — 90° .

Picrate of isoapiole from dill oil, $C_{18}H_{17}O_{11}N_3$, crystallises from alcohol in intensely red, prismatic needles which melt at 81° .

Cryoscopic measurements of the last two picrates in acetophenone show that they are completely resolved into their constituents.

T. H. P.

Isomeric Ethers of Pyrogallol. JOSEF HERZIG and JACQUES POLLAK (*Monatsh.*, 1904, 25, 808—816. Compare Abstr., 1903, i, 89; this vol., i, 808).—Partial methylation of pyrogallol by means of a limited amount of potassium hydroxide and methyl iodide leads to the formation of a mixture of the methyl ethers which, on acetylation, yielded a mixture of the oily acetyl derivatives of the dimethyl ethers and the crystalline acetyl monomethyl ethers. Of the latter, that which is sparingly soluble in alcohol is 1:2-diacetoxy-3-methoxybenzene; the alcoholic mother liquors contain 1:3-diacetoxy-2-methoxybenzene, which forms monoclinic crystals, melts at 51—54°. 1:3-Dihydroxy-2-methoxybenzene, obtained by hydrolysis of the diacetyl derivative with dilute sulphuric acid, melts at 85—87° and boils at 154—155° under 24 mm. pressure. Hoffmann-La Roche's supposed 1:3-dihydroxy-2-methoxybenzene (*Chem. Centr.*, 1900, ii, 459) is probably 1:3-dihydroxy-4-methoxybenzene. G. Y.

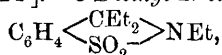
Chemical Action of Light. FRANZ SACHS and SIEGFRIED HILPERT (*Ber.*, 1904, 37, 3425—3431. Compare this vol., i, 156).—When a solution of *o*-nitrobenzyl alcohol in benzene is exposed to the action of light, it rapidly becomes yellowish-green and deposits a yellow, flocculent precipitate, which becomes almost black on prolonged exposure to light. The product, $C_7H_5O_2N$, is amorphous, commences to decompose at 237°, and is easily soluble in alcohol, glacial acetic acid, or aqueous ammonia. On acidification of its ammoniacal solution, it separates as a rose-coloured to dark brown flocculent precipitate; on addition of ether to the alcoholic solution, it is obtained as a violet powder. It is distinguished from azobenzoic acid by its indifference to reducing reagents. When a solution of *o*-nitrobenzyl alcohol and phenylhydrazine in glacial acetic acid is exposed to light, evolution of nitrogen takes place, and a product is obtained which forms a brownish-yellow, crystalline powder, sinters at 160°, and, when heated quickly, melts at 184°.

The action of light on *o*-nitrobenzaldehyde dissolved in hydrogen cyanide, or on *o*-nitromandelonitrile, leads to the formation of *o*-nitrosobenzoic acid. G. Y.

Action of Organomagnesium Compounds on Alkylated Saccharins. FRANZ SACHS, F. VON WOLFF, and AL. LUDWIG (*Ber.*, 1904, 37, 3252—3268. Compare this vol., i, 266).—*Phenyldimethylcarbinol-o-sulphonethylamide*, $OH \cdot CMe_2 \cdot C_6H_4 \cdot SO_2 \cdot NHEt$, prepared by the interaction of magnesium methyl bromide and "ethylsaccharin," crystallises in snow-white crystals melting at 109—110°; from ether, it crystallises in large, monoclinic crystals [$a : b : c = 0.9822 : 1 : 0.6324$; $\beta = 52^\circ 16'$]. When dissolved in concentrated sulphuric acid, the salt crystallising in large, colourless plates melting at 40° is formed; heating with fuming hydrogen chloride converts it into a *benzylsulphone* of the constitution $C_6H_4 \cdot \begin{smallmatrix} CMe_2 \\ \diagup \quad \diagdown \\ SO_2 \end{smallmatrix} \cdot O$, melting at 106—107°.

Phenyldiethylcarbinol-o-sulphonethylamide, $OH \cdot CEt_2 \cdot C_6H_4 \cdot SO_2 \cdot NHEt$, prepared from "ethylsaccharin" and magnesium ethyl bromide, crys-

tallises in large, colourless, monoclinic, holohedric crystals [$a:b:c = 0.914:1:0.577$; $\beta = 66^\circ 24'$]. *C-Diethyl-N-ethylbenzylsultam*,



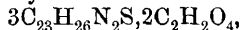
obtained on dissolving in sulphuric acid and precipitating with water, melts at $140\text{--}150^\circ$. *Benzyl-diethylsulphone*, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CEt}_2 \\ \diagup \quad \diagdown \\ \text{SO}_2 \end{array} \text{O}$, forms long, colourless, transparent, feather-like crystals melting at 91° .

Phenyl-diisopropylcarbinol-o-sulphonethylamide crystallises in needles melting at $117\text{--}118^\circ$. *Phenyl-diisoamylcarbinol-o-sulphonethylamide* forms large, flat prisms melting at $66\text{--}67^\circ$. *Triphenylcarbinol-o-sulphonethylamide* forms small, colourless prisms which melt at $184\text{--}185^\circ$. *C-Diphenyl-N-ethylbenzylsultam* melts at $155\text{--}165^\circ$, its *dinitro*-derivative melts between 220° and 230° , whilst the *diamino*-derivative, which forms yellow rhombohedra, becomes brown at 250° .

Phenyl-dimethylcarbinol-o-sulphonmethylamide melts at $105\text{--}106^\circ$ and forms thin, monoclinic prisms as much as 4 cm. long [$a:b:c = 0.9388:1:0.5918$; $\beta = 56^\circ 5'$]. *Phenyl-diethylcarbinol-O-sulphonmethylamide* melts at $111\text{--}112^\circ$ and separates in rhombic, holohedric, transparent crystals [$a:b:c = 0.9747:1:0.5959$]. *Phenyl-diisopropylcarbinol-O-sulphonmethylamide* crystallises in silvery tablets melting at $122\text{--}123^\circ$, the *diisoamyl* derivative melts at $81\text{--}82^\circ$ and separates in stepped, four-sided prisms similar to common salt. *Triphenylcarbinol-O-sulphonmethylamide* forms hexagonal prisms melting at $194\text{--}195^\circ$; *diphenylbenzylsulphone* melts at 210° . The crystallography of many of these compounds is described in detail. E. F. A.

Colourless Salts of Triphenylcarbinol and Diphenylcarbinol.

RUDOLF LAMBRECHT and HUGO WEIL (*Ber.*, 1904, 37, 3058—3062).—The colourless *oxalate* of the carbinol base of malachite-green, $\text{C}_{23}\text{H}_{26}\text{ON}_2 \cdot 2\text{C}_2\text{H}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$, prepared by mixing oxalic acid and the base at 0° , melts at 78° and on further heating is converted into the coloured oxalate, which has a metallic lustre, and melts at 110° . In a similar manner, tetramethyldiaminothiol forms a colourless *oxalate*,



which melts and decomposes at 140° ; this, when kept, or when heated in aqueous solution, is converted into the coloured oxalate of malachite-green.

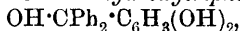
Tetramethyldiaminobenzhydrol forms a colourless zincochloride, $\text{C}_{21}\text{H}_{30}\text{ON}_2 \cdot \text{ZnCl}_2 \cdot 2\text{HCl}$; the aqueous solution becomes blue on heating, but colourless again when the solution is cooled. E. F. A.

Action of Triphenylcarbinol on Hydroxylamine. ARTHUR MOTHWURF (*Ber.*, 1904, 37, 3150—3152).—From the action of triphenylcarbinol on hydroxylamine, no definite product was obtained by Baeyer and Villiger (*Abstr.*, 1902, i, 769), but the author finds that, if the use of methyl alcohol as the crystallising agent be avoided, *bistriphenylmethylhydroxylamine*, $\text{C}_{38}\text{H}_{31}\text{ON}$, is obtained; it separates from benzene in rhombic crystals and melts at 184° . It is also formed when an excess of the carbinol chloride acts on hydroxylamine; it has neither acid nor basic characters, does not reduce

Fehling's solution, and does not form acyl or nitroso-derivatives. It is easily decomposed when boiled with acids and is probably a $\beta\beta$ -substituted hydroxylamine.

Triphenylmethylhydroxylamine, $C_{19}H_{17}ON$, prepared by the action of triphenylcarbinol chloride on an excess of hydroxylamine, separates from a mixture of benzene and light petroleum in tetragonal prisms with pyramidal ends and melts at $124-135^\circ$. It is a β -derivative, since it reduces cold Fehling's solution. It is a weak base and forms a *hydrochloride*, crystallising in needles; its *acetyl* derivative separates from light petroleum in hexagonal pyramids and melts at $98-102^\circ$.
A. McK.

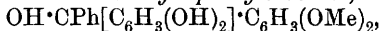
Hydroxyfuchsones. FRANZ SACHS and RICHARD THONET (*Ber.*, 1904, 37, 3327—3334).—3:4-*Dihydroxytriphenylcarbinol*,



prepared by the condensation of benzophenone chloride with catechol by means of concentrated sulphuric acid, forms a light yellow powder. When heated at $80-105^\circ$, it forms *quino-2-hydroxyfuchsones*, $CPh_2 \cdot C_6H_3O \cdot OH$, a dark orange-coloured powder, melting at 123° (compare Baeyer and Villiger, this vol., i, 786). The dyeing properties of the latter substance are interesting since it does not contain two hydroxyl groups in the ortho-position relatively to one another: its behaviour with mordants varies; with some it dyes marked colours, whilst with others there is little result.

Catecholdiphenylmethyle ether, $CPh_2 \langle \overset{O}{\text{C}} \rangle C_6H_4$, prepared by gently heating catechol with benzophenone chloride without the presence of a condensing agent, separates from alcohol in colourless prisms and melts at 93° .

3:4-*Dihydroxy-3':4'-dimethoxytriphenylcarbinol*,



prepared by the action of benzoylveratrol chloride on catechol in the presence of aluminium chloride, melts at $73-74^\circ$; when heated at 80° , it is converted into its *fuchsones*.

When the chloride of Michler's ketone is condensed with catechol in the presence of sulphuric acid, Liebermann's proto-blue (tetramethyldiamino-3:4-dihydroxytriphenylcarbinol) is formed (compare Abstr., 1903, i, 861).

3:4-*Dimethoxytriphenylcarbinol*, $OH \cdot CPh_2 \cdot C_6H_3(OMe)_2$, prepared by the action of magnesium phenyl bromide on benzoylveratrol, melts at 151.5° . When reduced by zinc and glacial acetic acid, it forms 3:4-*dimethoxytriphenylmethane*, $CHPh_2 \cdot C_6H_3(OMe)_2$, melting at 110.5° .

3:4-*Dimethoxytriphenylchloromethane*, $CPh_2Cl \cdot C_6H_3(OMe)_2$, prepared by passing hydrogen chloride into a chloroform solution of dimethoxytriphenylcarbinol, melts at 148.5° . When slowly heated at 140° , it decomposes with formation of methyl chloride and a reddish-brown product, presumably the corresponding methoxyfuchsones. When dimethoxytriphenylcarbinol is heated with aniline and benzoic acid, the methoxy-groups are replaced by aniline groups, violet-red dyes being produced.
A. McK.

Tri-*p*-tolylcarbinol. ARTHUR MOTHWURF (*Ber.*, 1904, 37, 3153—3163. Compare Gomberg, this vol., i, 489).—According to Baeyer and Villiger (*Abstr.*, 1902, i, 769), the basicity of triphenylcarbinol is increased by the introduction of methoxyl groups; since the oxonium theory renders it probable that these basic characters are conditioned by the unsaturated nature of the oxygen atom, the author has studied tri-*p*-tolylcarbinol and finds that the introduction of the three methyl groups into triphenylcarbinol has much the same effect in increasing the basic character of the latter as has the introduction of a methoxyl group in the para-position.

Tri-*p*-tolylcarbinol (compare Gomberg, *loc. cit.*) was prepared from methyl *p*-toluate and magnesium *p*-tolyl iodide; when the oil, obtained after removal of the ether used as the solvent in this Grignard reaction, was dissolved in glacial acetic acid, tri-*p*-tolylcarbinyll acetate, separating in prisms and melting indefinitely at 87°, was obtained; by the action of dilute sodium hydroxide, it yields tri-*p*-tolylcarbinol, which melts at 96.5°, and with boiling glacial acetic acid forms a yellowish-green solution, and with concentrated sulphuric acid a greenish-red solution.

Tri-*p*-tolylmethane, prepared by the reduction of tri-*p*-tolylcarbinol with zinc dust and hydriodic acid, forms monoclinic prisms and melts at 53—54°. Tri-*p*-tolylcarbinyll chloride melts at 181°, whilst Gomberg gives 173°. Tri-*p*-tolylchloromethane aluminium chloride, $C_{22}H_{21}Cl, AlCl_3$, forms yellowish-green needles, which are instantly decomposed by water. Tri-*p*-tolylcarbinyll bromide forms yellow rhombohedra and melts at 161—163°. Tri-*p*-tolylcarbinyll iodide forms dark blue needles. Tri-*p*-tolylcarbinyll ethyl ether melts at 114°, whilst Gomberg gives 105°.

Tri-*p*-tolylacetoneitrile, prepared by the action of mercuric cyanide on tri-*p*-tolylcarbinyll chloride, separates in rhombohedra and melts at 192°. Tri-*p*-tolylcarbinyll thiocyanate crystallises from ethyl acetate in needles and melts at 147—148°.

Sodium tri-*p*-tolylmethanesulphonate, prepared by adding a few drops of sulphuric acid and then sodium hydrogen sulphite to an alcoholic solution of tri-*p*-tolylcarbinol, forms silky needles and contains $1H_2O$.

Tri-*p*-tolylcarbinyllamine, prepared by passing dry ammonia into a benzene solution of tri-*p*-tolylcarbinyll chloride, separates from a mixture of benzene and light petroleum in monoclinic prisms and melts at 97°; it is readily decomposed when boiled with water. Its acetyl derivative melts at 211°.

Tri-*p*-tolylcarbinol anilide (tri-*p*-tolylcarbinyllaniline), prepared from tri-*p*-tolylcarbinyll chloride and aniline, separates from light petroleum in rhombic prisms and melts at 131°.

Benzeneazotri-*p*-tolylmethane, $Ph \cdot N_2 \cdot C(C_6H_4Me_3)_3$, prepared by the action of phenylhydrazine on tri-*p*-tolylcarbinol, separates from methyl alcohol in yellow prisms and melts and decomposes at 113—116°. Benzenehydrazotri-*p*-tolylmethane is the initial product of the preceding action, but is rather unstable.

β -Tri-*p*-tolylmethylhydroxylamine forms monoclinic prisms and melts at 103—105°, is readily decomposed by acids, and reduces Fehling's solution. Its acetyl derivative melts at 157°. Bistri-*p*-tolylmethylhydroxylamine separates from light petroleum in needles and melts at 155°.

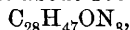
Although triphenylcarbinol does not yield crystalline nitro-derivatives (Baeyer and Villiger, Abstr., 1903, i, 811), tri-*p*-tolylcarbinol does. *Trinitrotri-p-tolylcarbinol*, prepared by nitrating with 68 per cent. nitric acid in the cold, crystallises from benzene in tetragonal prisms and melts at 162°. It does not form a chloride, nor does it combine with sodium hydrogen sulphite.

Hexanitrotri-p-tolylcarbinol, prepared by allowing tri-*p*-tolylcarbinol to remain in contact with fuming nitric acid for 12 hours, forms monoclinic prisms and melts at 253°. *Hexanitrotri-p-tolylmethane*, prepared from tri-*p*-tolylmethane in an analogous manner, forms monoclinic prisms and melts at 280°.

A. MCK.

Cholesterol. II. OTTO DIELS and EMIL ABDERHALDEN (*Ber.*, 1904, 37, 3092—3103. Compare Abstr., 1903, i, 819).—The acid formerly supposed to have the composition $C_{20}H_{32}O_3$ (*loc. cit.*) has in reality the formula $C_{27}H_{44}O_4$, and behaves on titration with potassium hydroxide as a dibasic acid; when titrated with sodium hydroxide, however, it appears to be a monobasic acid, owing to the formation of a very sparingly soluble mono-sodium salt. The silver salt formerly described has the formula $C_{27}H_{44}O_4Ag_2$, and the ethyl ester is an acid ester having the composition $C_{29}H_{48}O_4$. A double linking probably exists in the acid, but the behaviour of the latter with bromine or potassium permanganate is not conclusive. The dimethyl ester of the acid, prepared from the silver salt, crystallises from methyl alcohol in white prisms, sinters at 67°, and melts at 69°; the monomethyl ester, prepared by direct methylation, crystallises from acetone in thick, six-sided plates and melts at 125° (corr.).

Cholestenone, $C_{27}H_{44}O$, obtained by adding finely-powdered copper oxide to fused cholesterol, separates from methyl alcohol in well-formed, white crystals and melts at 78°; the phenylhydrazone, $C_{33}H_{50}N_2$, crystallises from ethyl acetate in yellow needles, sinters at 142°, and melts at 152°; the *p*-nitrophenylhydrazone, $C_{33}H_{49}O_2N_3$, crystallises from boiling acetone in orange-yellow prisms, softens at 160°, and melts indefinitely at about 195°. The semicarbazone,



separates from methyl alcohol in slender crystals, sinters at 222°, and melts at 240° (corr.). With hydroxylamine, cholestenone behaves as an $\alpha\beta$ -unsaturated ketone. In warm weather, the two substances condense in methyl-alcoholic solution to form the oxime, $C_{27}H_{45}ON$, which crystallises from ethyl acetate and melts at 152° (corr.); in cooler weather, however, hydroxylamine becomes attached at the double linking to form the additive-compound, $C_{27}H_{47}O_2N$, which crystallises from acetone in small, four-sided plates and melts indefinitely between 142° and 147°. On warming the additive compound with dilute hydrochloric acid, the normal oxime is obtained.

Cholesteryl chloride is best prepared by mixing cholesterol with thionyl chloride.

W. A. D.

Preparation of cycloCitrylideneacetic Acid and its Derivatives. ALBERT VERLEY (D.R.-P. 153575).—Citrylideneacetic acid and its esters and nitrile are not converted into cyclo-derivatives by

the usual agents employed for the conversion of ψ -ionone into ionone. The conversion is, however, readily effected by means of syrupy phosphoric acid containing 6—8 per cent. of sulphuric acid at 35°. *cyclo-Citrylideneacetic acid* forms a viscid syrup, becoming crystalline after several months.

Methyl citrylideneacetate, $C_{13}H_{20}O_2$, prepared from methyl hydrogen malonate, citral, and pyridine at 100° (compare Abstr., 1899, i, 768), boils at 133° under 16 mm. pressure. *Methyl cyclocitrylideneacetate*, a colourless liquid with odour of mignonette, boils at 138° under 17 mm. pressure; the *ethyl* ester boils at 141° under 17 mm. pressure and has an odour of violets. *cycloCitrylideneacetoneitrile* is a yellow liquid boiling at 141° under 17 mm. pressure; its odour resembles that of ionone. C. H. D.

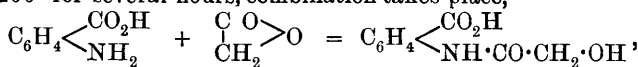
Molecular Weights of the Yellow Nitroso-compounds. FREDERICK J. ALWAY and ROSS A. GORTNER (*Amer. Chem. J.*, 1904, 32, 400—403).—It has been shown by Alway and Bonner (Abstr., 1903, i, 764) that *p*-nitrosobenzaldehyde, which has a yellow colour, has a normal molecular weight in freezing and boiling benzene and in freezing acetic acid solutions.

The molecular weights of methyl and ethyl *p*-nitrosobenzoates, ethyl *m*-nitrosobenzoate, and methyl and ethyl *p*-nitrosocinnamates in solution in benzene have been determined by the cryoscopic method. The results obtained with the *p*-nitrosocinnamates are not conclusive, since the quantities employed were very small; the ethyl ester formed a greenish-yellow solution and produced a depression of the freezing point corresponding with 50 per cent. in the unimolecular and 50 per cent. in the bimolecular condition, whilst the methyl ester formed a yellow solution and gave a result corresponding with the bimolecular condition. The *p*-nitrosobenzoates showed the normal molecular weight.

Ethyl m-nitrosobenzoate, $NO \cdot C_6H_4 \cdot CO_2Et$, obtained by reducing ethyl *m*-nitrobenzoate with zinc dust and acetic acid and treating the product with ferric chloride, forms stellate groups of white crystals and melts at 52—53° to a green liquid. It exists in solution chiefly in the unimolecular condition, but at the temperature of freezing benzene a small proportion is present in the bimolecular condition.

E. G.

[*o*-Glycollylaminobenzoic Acid and the Synthesis of Indigo.] FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 153576 and 153577).—On fusing together anthranilic acid and glycollide at 180—200° for several hours, combination takes place,



forming *o*-glycollylaminobenzoic acid, which melts at 167° and dissolves readily in hot water or organic solvents. Dilute acids or alkali hydroxides hydrolyse it on warming to glycollic and anthranilic acids.

o-Glycollylaminobenzoic acid is converted, on fusion with alkali hydroxide at 230—300°, into a mixture of indoxyl and an indoxyl-carboxylic acid in proportions varying with the conditions of the

fusion. A satisfactory yield of indigo is obtained on oxidising the product.
C. H. D.

Benzamidesulphonic Acid. A. BÜHNER (*Annalen*, 1904, 333, 283—288).—On attempting to prepare acetylbenzamide by the action of acetic anhydride on benzamide in the presence of sulphuric acid, an unstable compound, the *benzamide* salt of benzamidesulphonic acid, $\text{NHBz} \cdot \text{SO}_3\text{H} \cdot \text{NH}_2\text{Bz}$, was formed. The free acid is unstable, but forms a series of stable salts and basic salts. It is decomposed into potassium phenyl sulphate by heating with potassium hydroxide, and by heating with aniline at $150\text{--}160^\circ$ into benzanilide and ammonium phenylsulphamate, thus: $\text{NHBz} \cdot \text{SO}_3\text{H} \cdot \text{NH}_2\text{Ph} + \text{NH}_2\text{Ph} = \text{NHBzPh} + \text{NH}_2 \cdot \text{SO}_3\text{H} \cdot \text{NH}_2\text{Ph} \rightarrow \text{NHPhSO}_3 \cdot \text{NH}_4$, two phases being recognised in the reaction.

The benzamide salt is prepared by adding benzamide to a cooled mixture of acetic anhydride and sulphuric acid; the temperature at first rises, and then the salt crystallises out; it melts at $145\text{--}146^\circ$. Its solution in ice-cold water is at first clear, but in a short time benzamide separates; if the latter is extracted with ethyl acetate and silver nitrate added to the solution, which has been carefully neutralised with sodium hydroxide, the *basic silver* salt of benzamidesulphonic acid, $\text{C}_7\text{H}_5\text{O}_4\text{NSAg}_2$, crystallises out in colourless leaflets. The normal *silver* salt, $\text{C}_7\text{H}_6\text{O}_4\text{NSAg}$, is prepared by warming a solution of the acid with silver oxide until it is neutral, adding acetone, filtering, and evaporating the filtrate to dryness under reduced pressure; it forms leaflets. Aniline benzamidesulphonate is prepared by adding aniline to an aqueous solution of the acid and evaporating to dryness; the salt melts at 120° .
K. J. P. O.

Alkylation of Acid Amides. A. BÜHNER (*Annalen*, 1904, 333, 289—295).—When acid amides are treated with methyl sulphate at moderate temperatures, an additive compound is formed, which appears to be the salt of methyl hydrogen sulphate and an imino-ether; thus from benzamide is formed the salt $\text{OMe} \cdot \text{CPh} \cdot \text{NH}_2 \cdot \text{O} \cdot \text{SO}_3\text{Me}$. In many cases the salt cannot be isolated in a pure state. It is suggested that this reaction is a case of 1:3-addition, in which the double linking between the carbon atom and the oxygen becomes a single linking, and the nitrogen becomes quinquivalent and doubly linked to the carbon.

Mol. proportions of benzamide and methyl sulphate are heated on the water-bath in benzene solution and the salt precipitated with alcohol; it crystallises in hygroscopic needles melting at $108\text{--}111^\circ$, and gives no precipitate with barium chloride; by alkali hydroxides, it is converted into benziminomethyl ether, boiling at $95\text{--}97^\circ$ under $14\text{--}15$ mm. pressure.

Methylbenzamide behaves in a similar manner, but the *additive* product is a viscid oil, from which the unstable methylated benziminomethyl ether can be obtained in a pure state.

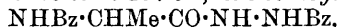
The *additive* compound, $\text{OMe} \cdot \text{CMe} \cdot \text{NHPh} \cdot \text{O} \cdot \text{SO}_3\text{Me}$, prepared in a similar manner from acetanilide and methyl sulphate, is a very hygroscopic salt melting at $80\text{--}82^\circ$, and immediately decomposed into

methyl acetate and aniline methyl sulphate by water. The salt is converted into acetanilidomethyl ether by treatment with dry sodium carbonate in chloroform solution; the ether boils at 81—82° under 12 mm. pressure (compare Lander, *Trans.*, 1901, 79, 691) and reacts with aniline giving diphenylethaneamidine (m. p. 131—132°).

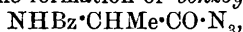
Dimethylbenzamide and methylacetanilide yield oily additive products, whilst anthranil gives a very unstable, red, crystalline substance.

K. J. P. O.

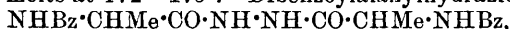
Condensations with Amino-acids. V. Combination of Alanine and Glycine by means of Benzoylalanineazide. THEODOR CURTIUS and CHARLES FLORENT VAN DER LINDEN (*J. pr. Chem.*, 1904, [ii], 70, 137—157. Compare Curtius and Lambotte, this vol., i, 835).—*Benzoylalanylhydrazide*, $\text{NHBz}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{N}_2\text{H}_3$, obtained by shaking ethyl benzoyl- α -aminopropionate with hydrazine hydrate in ethereal solution, crystallises in colourless needles and melts at 105—107°; the *hydrochloride* crystallises in slender needles; the *benzylidene* derivative, $\text{NHBz}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CHPh}$, forms needles and melts at 194°; the β -*propylidene* derivative, $\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}_3\cdot\text{CMe}_2$, crystallises from water in needles which melt at 75—80°; after drying over sulphuric acid, it melts at 157·5°; the *benzoyl* derivative,



formed by the Schotten-Baumann reaction, crystallises in needles and melts at 180—184°. The action of sodium nitrite and acetic acid on the hydrazide leads to the formation of *benzoylalanylazoimide*,



which forms a white, crystalline powder, melts at 54°, decomposes at 55°, detonates when heated on platinum, and dissolves in dilute sodium hydroxide to a momentarily bluish-yellow, fluorescent solution. When boiled with absolute methyl alcohol, the azoimide forms the *methylurethane*, $\text{NHBz}\cdot\text{CHMe}\cdot\text{NH}\cdot\text{CO}_2\text{Me}$, which crystallises in snowy needles and melts at 150°; the *ethylurethane*, formed by boiling the azide with ethyl alcohol, crystallises in white needles and melts at 140°. When boiled with aniline in ethereal solution, the azoimide forms the *anilide*, $\text{NHBz}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NHPh}$, which crystallises in white needles and melts at 163—165°; the *p-toluidide* forms glistening leaflets or needles and melts at 172—175°. *Dibenzoylalanylhydrazide*,



obtained in the aqueous filtrate from the azoimide, and by the action of iodine on benzoylalanylhydrazide in alcoholic solution, crystallises in colourless, slender needles and melts at 262°.

Benzoylalanylalanine, $\text{NHBz}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, obtained by the action of benzoylalanylazoimide on alanine in concentrated aqueous and slightly alkaline solution, crystallises in colourless needles and melts at 170—171°; the *ethyl* ester is prepared by heating the silver salt with ethyl iodide, or, along with the ethyl ester of benzoylalanine, by shaking the acid with 1—3 per cent. alcoholic hydrogen chloride; both methods give a very small yield of the ester; it crystallises in colourless needles and melts at 148—149°.

Benzoylalanylalanylhydrazide,

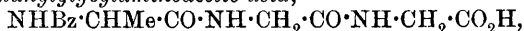


crystallises in needles and melts at 183—184°; the *benzylidene* derivative is a colourless, flocculent, crystalline substance; it melts, with slight decomposition, at 230°. The *azoimide* was obtained in very small quantity; it detonates when heated on platinum.

Benzoylalanylaminooacetic acid, $\text{NHBz}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, obtained by acting with benzoylalanylazoimide on glycine in slightly alkaline aqueous solution, crystallises in slender, colourless needles, melts at 166°, and gives no biuret reaction with Fehling's solution. The aqueous solution of the *ammonium* salt gives a granular, blue precipitate, $(\text{C}_{12}\text{H}_{13}\text{O}_4\text{N}_2)_2\text{Cu}$, with copper sulphate, a white precipitate, $\text{C}_{12}\text{H}_{13}\text{O}_4\text{N}_2\text{Ag}$, with silver nitrate, a reddish-brown precipitate with ferric chloride, and, after some hours, a white precipitate with barium chloride.

The *ethyl* ester crystallises in clusters of needles and melts at 108°; the *hydrazide* crystallises in slender, colourless needles and melts at 161—162°; the *benzylidene* derivative of the hydrazide forms colourless needles and melts at 226°; the β -*propylidene* derivative of the hydrazide crystallises in small, colourless needles and melts at 177°; the *azoimide*, which is a crystalline powder and melts and decomposes at 84°, is formed along with a substance which is probably dibenzoylalanylglycylhydrazide and melts at a high temperature.

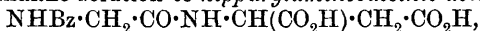
Benzoylalanylglycylaminooacetic acid,



formed from benzoylalanylglycylazoimide and glycine, or from benzoylalanylazoimide and glycylglycine hydrochloride, crystallises in colourless needles, melts and becomes brown at 204—205°, and gives the biuret reaction with Fehling's solution; the *silver* salt is a crystalline powder.

G. Y.

Condensations with Amino-acids. VI. Formation of Compounds of Aspartic Acid by means of Hippurylazoimide. THEODOR CURTIUS and HANS CURTIUS (*J. pr. Chem.*, 1904, [ii], 70, 158—194).—Hippurylazoimide condenses with aspartic acid in aqueous alkaline solution to *hippurylaminosuccinic acid*,



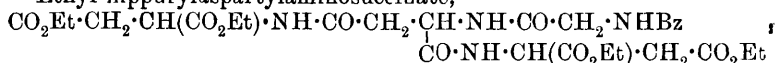
which crystallises from hot water in strongly refractive, thick prisms and melts at 191°; the *silver* salt, $\text{C}_{13}\text{H}_{12}\text{O}_6\text{N}_2\text{Ag}_2, 1\frac{1}{2}\text{H}_2\text{O}$, decomposes on exposure to light or when boiled with water; the *barium* salt, $\text{C}_{13}\text{H}_{12}\text{O}_6\text{N}_2\text{Ba}$, remains unchanged at 260°; the *dihydrazine* salt, $\text{C}_{13}\text{H}_{14}\text{O}_6\text{N}_2, 2\text{N}_2\text{H}_4$, forms a white, flocculent precipitate and melts at 168—170°; the *copper* salt, $\text{C}_{13}\text{H}_{12}\text{O}_6\text{N}_2\text{Cu}, 3\text{H}_2\text{O}$, is blue when freshly prepared, green when dried. The *diethyl* ester, $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, is obtained either by the action of alcoholic hydrogen chloride on hippurylaminosuccinic acid or by the condensation of hippurylazoimide with diethyl aminosuccinate; it forms a white, crystalline powder and melts at 92°. The action of ethyl iodide on the silver salt leads to the formation of a viscid, red *syrup*, which in aqueous solution is colourless at the ordinary temperature, but at about 10° forms a blue jelly; if the solution is boiled until the evolution of iodine is complete, the colour reaction does not take place on cooling. The *dimethyl* ester is obtained

either by boiling the acid with methyl-alcoholic hydrochloric acid or by heating the silver salt with methyl iodide; it melts at 136° . If hydrazine hydrate is added to a boiling alcoholic solution of the dimethyl ether, the *dihydrazide*, $C_9H_8O_2N \cdot NH \cdot CH(CO \cdot N_2H_3) \cdot CH_2 \cdot CO \cdot N_2H_3$, is formed; it separates from a concentrated aqueous solution in anhydrous crystals, from a dilute solution in crystals containing 1 mol. of water of crystallisation, and melts at 213.5° ; the *hydrochloride*, $C_{13}H_{18}O_4N_6 \cdot 2HCl$, decomposes at 125° ; the *dibenzylidene* derivative melts at 204° ; the *di-o-hydroxybenzylidene* derivative forms a voluminous, red precipitate and melts at 209° ; the *di-β-propylidene* derivative melts and decomposes at 183° ; the *dibenzoyl* derivative,

$NHBz \cdot CH_2 \cdot CO \cdot NH \cdot CH(CO \cdot N_2H_2Bz) \cdot CH_2 \cdot CO \cdot N_2H_2Bz$, melts at 228° . The *diazoimide* is obtained by dissolving the dihydrazide in dilute hydrochloric acid and adding a concentrated solution of sodium nitrite to the well-cooled mixture; it melts at about 70° , decomposes suddenly when more highly heated, and dissolves in aqueous alkali hydroxides to a yellowish-red solution. When boiled with absolute alcohol until the evolution of nitrogen is completed, the diazoimide yields the *urethane*,

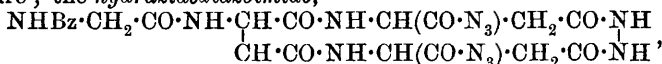
$NHBz \cdot CH_2 \cdot CO \cdot NH \cdot CH(NH \cdot CO_2Et) \cdot CH_2 \cdot NH \cdot CO_2Et$, which melts at 214° and on digestion with dilute sulphuric acid evolves carbon dioxide, and, with phenylhydrazine, yields glyoxal-phenylosazone. When boiled with water, the diazoimide yields carbon dioxide, nitrogen, and a sparingly soluble precipitate. The *diamide*, formed by the action of ammonia on the diazoimide in ethereal or aqueous solution, crystallises in nacreous leaflets and melts and decomposes at 223° . The action of aniline on the diazoimide in ethereal solution leads to the formation of the *phenylcarbamide-anilide* derivative, $NHBz \cdot CH_2 \cdot CO \cdot NH \cdot CH(CO \cdot NHPh) \cdot CH_2 \cdot NH \cdot CO \cdot NHPh$, which is obtained as a white powder and melts and decomposes at $218-220^{\circ}$. This product was heated with concentrated hydrochloric acid at 100° and the residue left on evaporation benzoylated by the Schotten-Baumann reaction; after extraction with light petroleum and water, the residue melted at 195° and was identical with Klebs' di- $\alpha\beta$ -benzoylaminopropionic acid (Abstr., 1894, i, 439). The similar *derivative* obtained by the action of *p*-toluidine on the diazoimide melts at 216° .

Ethyl hippurylaspartylaminosuccinate,



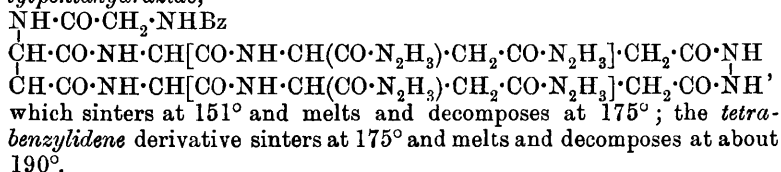
obtained by acting with dry hippurylaspartylidiazimide on ethyl aminosuccinate in ethereal solution. It forms a white powder, melts under 150° , gives the biuret reaction, and contains less than 1 mol. of hydrazic acid, which is completely eliminated only on hydrolysis of the ester with an alkali hydroxide or baryta. The *acid*, $C_{21}H_{24}O_{12}N_4$, forms colourless, transparent, glistening crystals, becomes yellow at 80° , melts and decomposes at about 100° , and on prolonged boiling with aqueous baryta is partially hydrolysed to hippurylaspartic acid and aspartic acid. The *silver* salt, $C_{21}H_{20}O_{12}N_4Ag_4$, decomposes at about 172° ; the *barium* salt, $C_{21}H_{20}O_{12}N_4Ba_2$, and the *lead* salt are described. The *tetrahydrazide*, $C_{21}H_{20}O_8N_4(N_2H_3)_4$, is a white powder, melts and

decomposes at 176° , and reduces ammoniacal silver solutions or Fehling's solution; the *tetrabenzylidene* derivative commences to sinter at 150° , and melts and decomposes, but not sharply, at a higher temperature; the *hydrazidediazoimide*,



obtained by the action of hydrochloric acid and sodium nitrite on the tetrahydrazide, decomposes when heated on platinum, or when boiled with alcohol or water, and with aniline in ethereal solution yields a *hydrazidedianilide*, which decomposes at about 147° , and when heated with hydrochloric acid at 160° yields benzylideneazaine on being shaken with benzaldehyde.

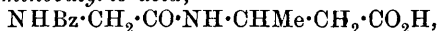
The hydrazidediazoimide and ethyl aminosuccinate form a white product, which evolves hydrazoic acid when hydrolysed by an alkali hydroxide and distilled with sulphuric acid. With hydrazine hydrate in alcoholic solution, the white product forms *hippuryl diaspartylaspartylpentahydrazide*,



Hippurylaspartyl diazoimide condenses with ethyl aminoacetate to ethyl hippurylaspartyl diaminoacetate, which melts at 195° . Hippurylazoimide and ethyl aminoacetate react in ethereal solution to form ethyl hippurylaminoacetate. G. Y.

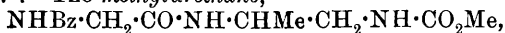
Condensations with Amino-acids. VII. Formation of Derivatives of β -Amino- α -hydroxypropionic Acid and of β -Aminobutyric Acid by means of Hippurylazoimide. THEODOR CURTIUS and OTTO GÜMLICH (*J. pr. Chem.*, 1904, [ii], 70, 195—223).—The action of hippurylazoimide on β -amino- α -hydroxypropionic acid in aqueous alkaline solution leads to the formation of *a-hippuroxy- β -aminopropionic acid*, $\text{NHBz} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{O} \cdot \text{CH}(\text{CH}_2 \cdot \text{NH}_2) \cdot \text{CO}_2\text{H}$, which crystallises in stellate groups of white needles, melts at 176° , and gives the characteristic primary amine reactions; the *ammonium* and *silver* salts are described. The action of alcoholic hydrogen chloride leads to hydrolysis of the hippuroxy-group and formation of ethyl hippurate. Ethyl- α -hippuroxy- β -aminopropionate is formed by the action of ethyl iodide on the silver salt; it crystallises in slender needles and melts at 96° .

Hippuryl- β -aminobutyric acid,



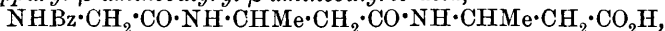
obtained by treating β -aminobutyric acid with hippurylazoimide in alkaline solution, crystallises in sheaves of needles and melts at 122° ; the *ammonium* salt forms white scales; the *silver* salt crystallises in sheaves of long needles; the *methyl* ester, obtained by boiling the acid with alcoholic hydrochloric acid, crystallises in colourless needles and melts at 104° ; the *ethyl* ester crystallises in sheaves of needles and melts at 80° .

Hippuryl-β-aminobutyrylhydrazide crystallises in sheaves of long, colourless needles, melts at 188°, and reduces ammoniacal silver or Fehling's solution; the *hydrochloride* is hygroscopic and melts at 188°; the *benzylidene* derivative forms granular crystals and melts at 154°; the *o-hydroxybenzylidene* derivative crystallises in glistening leaflets and melts at 186°; the *β-propylidene* derivative forms a yellow, crystalline mass or white, glistening leaflets and melts at 145°. *Ethyl hippuryl-β-aminobutyrylhydrazidoacetoacetate*, obtained by shaking the hydrazide with ethyl acetoacetate, melts at 142°, and yields ethyl acetoacetate and the hydrazide when boiled with water. *s-Hippuryl-β-aminobutyrylhydrazide*, $(\text{NHBz} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CO})_2 \text{N}_2 \text{H}_2$, obtained by boiling the primary hydrazide with alcohol in presence of iodine, crystallises in white leaflets, begins to decompose at 255°, and melts at 264°. *Hippuryl-β-aminobutyrylazoimide* forms a finely-divided powder and decomposes suddenly at 73°. The *anilide*, obtained by acting with aniline on the azoimide in alcoholic solution, melts at 206°; the *amide* crystallises in white leaflets and melts at 173°. The *carbamide*, $(\text{NHBz} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{NH})_2 \text{CO}$, formed when the azoimide is boiled with water, crystallises in colourless needles and melts at 157°. The *methylurethane*,



crystallises in colourless needles and melts at 151°; the *ethylurethane* crystallises in long needles and melts at 151°; when heated with concentrated hydrochloric acid at 110°, it is hydrolysed to benzoic acid, glycine, carbon dioxide, ethyl alcohol, and propylenediamine, which was characterised by conversion into its hydrochloride melting at 220° (Stache, Abstr., 1888, 1172). The *benzylurethane*, obtained from hippuryl-β-aminobutyrylazoimide and benzyl alcohol, crystallises in colourless needles and melts at 152–153°.

Hippuryl-β-aminobutyryl-β-aminobutyric acid,



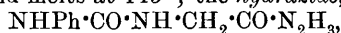
obtained by treating β-aminobutyric acid with hippuryl-β-aminobutyrylazoimide in alkaline aqueous solution, crystallises in white leaflets and melts at 147°; the *ammonium* salt forms a white, crystalline mass; the *silver* salt crystallises in slender needles; the *ethyl* ester, obtained by boiling the acid with alcoholic hydrogen chloride, crystallises in white leaflets and melts at 103°; the *hydrazide* crystallises in white leaflets and melts at 194°; its hydrochloride forms a voluminous, flocculent, hygroscopic mass and melts at 194°. *Hippuryl-β-aminobutyryl-β-aminobutyrylazoimide* forms a finely-divided, yellow powder and decomposes suddenly at 78°. G. Y.

Condensations with Amino-acids. VIII. Hippuryl-γ-amino-butyric Acid and Hippuryl-β-phenyl-α-alanine. THEODOR CURTIUS and ERNST MÜLLER (*J. pr. Chem.*, 1904, [ii], 70, 223–229).—*Hippuryl-γ-aminobutyric acid*, $\text{NHBz} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2 \text{H}$, formed by the action of hippurylazoimide on γ-aminobutyric acid, crystallises in delicate needles and melts at 176°; the *ammonium* salt forms colourless crystals and melts at 161–162°; the *silver* salt is obtained as a flocculent precipitate; the *ethyl* ester, formed by the alcoholic hydrogen chloride method, crystallises in colourless needles and melts

at 94°; the *hydrazide* crystallises in colourless, microscopic plates and melts and decomposes at 165—167°.

Hippuryl-β-phenylalanine, $\text{NHBz} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}(\text{CH}_2\text{Ph}) \cdot \text{CO}_2\text{H}$, obtained from β -phenylalanine (Erlenmeyer, Abstr., 1893, i, 581) and hippurylazoimide, crystallises in stellate groups of needles and melts at 172°; the *silver* salt is sensitive to light; the *ethyl* ester forms colourless needles and melts at 98°; the *hydrazide* crystallises in stellate groups of long needles, melts at 183°, and forms a *hydrochloride* which melts and decomposes at 186°; the *benzylidene* derivative melts at 158°; the *azoimide* decomposes at 70°. G. Y.

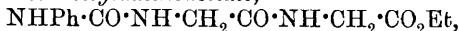
Condensations with Amino-acids. IX. The Action of Acylazoimides on Carbamide, and of Phenylcarbamic Azoimide on Glycine. THEODOR CURTIUS and WOLFGANG LENHARD (*J. pr. Chem.*, 1904, [ii], 70, 230—262. Compare Abstr., 1883, 337; 1896, i, 143, 647).—The action of hippurylazoimide on carbamide in various proportions leads to the formation of hippuric acid, but not of hippurylcarbamide; in one experiment, dibenzamidodihydroxytetrene (Rügheimer, Abstr., 1889, 249) was obtained. Benzoylcarbamide could not be obtained by acting with benzoyl chloride or benzoylazoimide on carbamide in slightly alkaline aqueous solution. Benzoylcarbamide and hydrazine hydrate do not enter into reaction in alcoholic solution, but on addition of benzoylcarbamide to hydrazine hydrate, an energetic reaction, resulting in the formation of benzoylhydrazide, takes place. Attempts to obtain condensation products by the action of phenylcarbamic azoimide (Abstr., 1899, i, 137) on carbamide and on biuret were without result. The action of phenylcarbamic azoimide on glycine in aqueous solution leads to the formation of phenylureid-acetic acid (Paal, Abstr., 1894, i, 332); the *methyl* ester crystallises in colourless prisms and melts at 143°; the *hydrazide*,



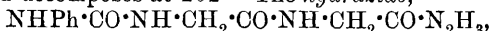
obtained by treating the methyl ester with hydrazine hydrate, crystallises in stellate groups of long needles and melts at 186.5°; the *hydrochloride*, $\text{C}_9\text{H}_{12}\text{O}_2\text{N}_4 \cdot \text{HCl}$, forms colourless, granular crystals and melts and decomposes at 191°; the *benzylidene* derivative crystallises in small, glistening leaflets and melts and decomposes at 227°; the *azoimide* crystallises in matted, delicate needles and melts and decomposes at 92°; the *amide*, $\text{NHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$, crystallises in stellate clusters of needles and melts at 201°; the *anilide* forms small, colourless needles and melts at 214°; the *nitrosoanilide*, obtained by the action of nitrous acid on the anilide, is a yellow powder and melts and decomposes at 131°; the *p-toluidide* crystallises in colourless needles and melts at 229°; the *derivative* from *m*-tolylene-diamine, $\text{NHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NH}_2$, forms matted, delicate needles and melts at 193°; the *phenylhydrazine* derivative, $\text{NHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NHPh}$, crystallises in long, glistening leaflets and melts at 227°. These amide and substituted amide derivatives are obtained by acting with the azoimide on the base. The *ethylurethane*, $\text{NHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO}_2\text{Et}$, prepared by boiling the azoimide with alcohol, crystallises in microscopic, colourless needles, melts at 190°, and, when boiled with dilute sulphuric acid,

yields carbon dioxide, formaldehyde, ammonia, and aniline. The *benzylurethane* crystallises in microscopic needles and melts at 204° .

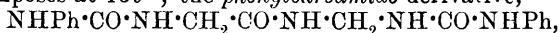
Ethyl phenylureidacetylaminooacetate,



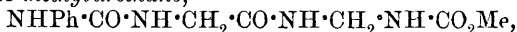
obtained by the condensation of phenylureidacetylazoimide with ethyl aminoacetate, crystallises in delicate, glistening leaflets, and melts at 165° . The *acid* is obtained by hydrolysing the ester with aqueous baryta or by adding phenylcarbamic azoimide to a solution of glycylglycine in aqueous sodium hydroxide; it crystallises in small, white needles and melts at 176° ; the *silver* salt crystallises in red needles and melts and decomposes at 202° . The *hydrazide*,



crystallises in small, colourless leaflets and melts and decomposes at 206° ; the *hydrochloride* forms a snow-white powder and melts and decomposes at 200° ; the *benzylidene* derivative is obtained as a sparingly soluble, flocculent precipitate; it melts and decomposes at 243° ; the β -*propylidene* derivative forms a crystalline powder and melts and decomposes at 234° . The *azoimide* forms a brittle, transparent mass and, when freshly prepared, melts and decomposes at 108° ; the *phenylhydrazide* crystallises in delicate, glistening leaflets and melts and decomposes at 139° ; the *phenylcarbamide* derivative,

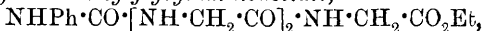


formed by the action of aniline on the azoimide, melts and decomposes at 222° ; the *methylurethane*,



melts and decomposes at 201° .

Ethyl phenylureidacetylglycylaminooacetate,



obtained by the condensation of phenylureidacetylaminooacetylazoimide with ethyl aminoacetate, crystallises in small, glistening leaflets and melts and decomposes at 203° . The *acid*, obtained by hydrolysis of the ester, crystallises in small leaflets, melts at 184° , and, when boiled with water, is decomposed with formation of phenylureidacetic acid. The *silver* salt is obtained as a white, very unstable precipitate. The *hydrazide* crystallises in small leaflets and melts and decomposes at 241° ; the *hydrochloride* is a white powder which melts and decomposes at 215° ; the *benzylidene* derivative is obtained as a white powder which melts at 247.5° . The *azoimide*, when quite freshly prepared, melts at $160-170^{\circ}$. The *ethylurethane* melts and decomposes at 244° , and yields formaldehyde and carbon dioxide when boiled with dilute sulphuric acid. G. Y.

m-Nitromethylenehippuric Acid. CHEMISCHE FABRIK AUF AKTIEN FORM. E. SCHERING (D.R.-P. 153860).—In a similar manner to methylenehippuric acid (this vol., i, 413), *m*-nitromethylenehippuric acid may be prepared by the action of paraformaldehyde and sulphuric acid on *m*-nitrohippuric acid. The acid crystallises from alcohol as a yellowish-white powder, melts at 165° , and dissolves in hot alcohol, benzene, or chloroform, but is insoluble in water or ether.

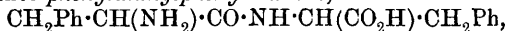
C. H. D.

Synthesis of Polypeptides. IV. Derivatives of Phenylalanine. EMIL FISCHER (*Ber.*, 1904, 37, 3062—3071. Compare *Abstr.*, 1903, i, 465, 607, 799, 800, and this vol., i, 652).—*α-Bromobenzylmalonic acid*, $\text{CH}_2\text{Ph}\cdot\text{CBr}(\text{CO}_2\text{H})_2$, prepared by brominating benzylmalonic acid, melts, when dry, at 137° (corr.) and crystallises from water in twinned prisms and from chloroform in six-sided plates. On heating this for $\frac{1}{2}$ — $\frac{3}{4}$ hour at 125 — 130° , *α-bromo-β-phenylpropionic acid*, $\text{CH}_2\text{Ph}\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$, is obtained in the form of an almost colourless oil, which, when heated with ammonia, forms phenylalanine. This affords an excellent practical method for the synthesis of this amino-acid. *α-Bromo-β-phenylpropionylchloride* is a colourless oil of unpleasant odour, boiling at 132 — 133° (corr.) under 12 mm. pressure, which, when condensed with glycylglycine in sodium hydroxide solution, forms *α-bromo-β-phenylpropionylglycylglycine*; this melts at 157 — 158° (corr.), and is soluble in 8 parts of hot water, from which it crystallises in prisms. *Phenylalanylglycylglycine*,



crystallises in oblique plates melting and decomposing at 235° (corr.). *Cinnamoylglycylglycine*, $\text{CHPh}\cdot\text{CH}[\text{CO}\cdot\text{NH}\cdot\text{CH}_2]_2\cdot\text{CO}_2\text{H}$, formed as a by-product when ammonia acts on *α-bromo-β-phenylpropionylglycylglycine*, melts at 229 — 235° (corr.) and crystallises in microscopic prisms. It can also be prepared by condensing cinnamoyl chloride with glycylglycine.

α-Bromo-β-phenylpropionyl-α-phenylalanine is formed to the extent of 35 per cent. of the theoretical quantity when phenylalanine is condensed with phenylbromopropionylchloride; it melts at 174 — 175° (corr.) and crystallises in colourless, octagonal plates. Ammonia converts it into *phenylalanylphenylalanine*,

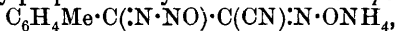


which crystallises from water, with $2\text{H}_2\text{O}$, in hexagonal prisms and melts and decomposes at 288° (corr.). As a by-product, *cinnamoylphenylalanine* is formed, which crystallises from alcohol in hexagonal plates melting at 198 — 199° (corr.), and is almost insoluble in water.

E. F. A.

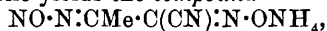
Dinitriles and Amyl Nitrite. JARL LUBLIN (*Ber.*, 1904, 37, 3467—3469. Compare Euler, this vol., i, 146, 230).—The compound obtained by E. von Meyer (*Abstr.*, 1895, i, 582) by the action of nitrous acid on benzeneacetodinitrile [*β*-imino-β-phenylpropionitrile] is shown to be the ammonium derivative of *α*-isonitroso-β-nitrosoimino-β-phenylpropionitrile, $\text{NO}\cdot\text{N}:\text{CPh}\cdot\text{C}(\text{CN})\cdot\text{N}\cdot\text{ONH}_4$. It is obtained by the action of amyl nitrite on an ethereal solution of the dinitrile. Part of the dinitrile undergoes decomposition yielding ammonia and the compound $\text{COPh}\cdot\text{C}(\text{CN})\cdot\text{N}\cdot\text{OH}$ (compare Meyer, *loc. cit.*). The ammonia and amyl nitrite then react with the remainder of the dinitrile yielding the ammonium salt.

β-Imino-β-*p*-tolylpropionitrile yields a similar compound,



melting and decomposing at 156° , and the ethereal mother liquor yields the compound $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{C}(\text{CN})\cdot\text{N}\cdot\text{OH}$, melting at 130.5 — 131° .

β -Iminobutyronitrile yields the compound



melting at 122°. β -Imino- β -phenyl- α -methylpropionitrile yields no such ammonium salt with amyl nitrite in ethereal solution. J. J. S.

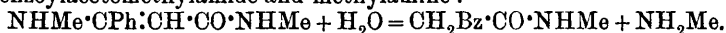
Nitrosocinnamic Acids and Esters. FREDERICK J. ALWAY and WALTER D. BONNER (*Amer. Chem. J.*, 1904, 32, 392—398).—*p*-Nitrosocinnamic acid, $\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$, prepared by reducing *p*-nitrocinnamic acid with zinc dust and acetic acid and treating the product with ferric chloride at a temperature of 40—60°, forms a yellow, indistinctly crystalline powder which, on heating, does not melt but darkens above 220°; when freshly prepared, it is soluble in alcohol or glacial acetic acid, but if left for several days, it becomes partly insoluble in alcohol. The *ethyl* ester crystallises in yellow needles, melts at 72—73°, and is soluble in alcohol, benzene, or acetic acid. The *methyl* ester crystallises in lemon-yellow needles and melts at 111—112° (uncorr.); it is sometimes obtained in green crystals, which, on exposure to light, are gradually converted into the yellow modification.

Ethyl *m*-nitrocinnamate is slightly more volatile with steam than the corresponding *p*-compound. *m*-Nitrosocinnamic acid crystallises in stellate groups of small, white needles, which gradually turn brown on exposure to moist air; on heating, it decomposes without melting at 230°. The *ethyl* ester crystallises in green, rhombic plates, melts at 65—66° (uncorr.), and is readily soluble in alcohol. E. G.

Transformation of β -Aminoamides into β -Ketoamides. ICILIO GUARESCHI (*Atti R. Accad., Torino*, 1903—1904, 39, 823—828).—The aminobenzylacetamide (β -aminocinnamide) previously prepared by the author (*Abstr.*, 1897, i, 168) crystallises in shining, colourless laminæ, exceedingly soluble in acetic acid and less so in water, alcohol, or ether. In solution, it has a neutral reaction and its aqueous or alcoholic solution is coloured violet-red by ferric chloride. Neither ferrous sulphate nor copper acetate precipitates it. It melts at 164.5—165°, and at higher temperatures sublimes, giving ammonia and a carbonaceous residue. When dissolved or suspended in water and treated with potassium nitrite solution and a trace of sulphuric acid, or when exposed in the solid state to the nitrous vapours from a mixture of potassium nitrite and sulphuric acid, it assumes a red colour. On heating with water, it takes up water and loses ammonia, yielding benzoylacetamide, which melts at 114—116°; Obregia gave the melting point 111—113° for this compound (*Abstr.*, 1892, 324).

Methylaminobenzylacetomethylamide (β -methylaminocinnamomethylamide), $\text{NHMe}\cdot\text{CPh}:\text{CH}\cdot\text{CO}\cdot\text{NHMe}$, obtained together with benzoylacetomethylamide by the interaction of methylamine and ethyl benzoylacetate, crystallises from ether in shining prisms and from alcohol in needles melting at 118—119°. It dissolves in water, but on boiling or evaporating the aqueous solution, an odour of methylamine is emitted. When exposed in the dry state to the action of nitrous vapours, it assumes a red colour, whilst with ferric chloride it

gives an intense violet coloration. On boiling with water, it yields benzoylacetomethylamide and methylamine :



Benzoylacetomethylamide, obtained as just described, crystallises in shining, heavy plates melting at 104—105°. In the solid state, it is not coloured by nitrous vapours, but ferric chloride produces an intense violet coloration.

T. H. P.

isocinnamic Acid. EMIL ERLÉNMEYER, jun. (*Ber.*, 1904, 37, 3361).—Recent publications by Michael (*Abstr.*, 1903, i, 418, 698) and by Liebermann (*Abstr.*, 1903, i, 255, 485) appear to cast doubt on the existence of *isocinnamic acid*, discovered by Erlenmeyer, sen.

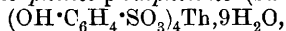
The author confirms his father's experiments. *isocinnamic acid* melting at 37° was isolated and the crystallographic measurements agreed with those formerly made by Haushofer.

isocinnamic acid readily undergoes change; thus, the clear crystals, when separated from their solution, become turbid, whilst the melting point also changes.

A. McK.

Thorium Salts of Certain Organic Acids. GILBERT T. MORGAN (*Pharm. J.*, 1904, [iv], 19, 472).—*Thorium salicylate*, *cinnamate*, and the three *coumarates* have been prepared by the interaction of the soluble alkali salts of the organic acids with thorium nitrate in aqueous solution. The *oleate*, prepared by mixing equivalent quantities of hydrated thorium oxide and oleic acid, has the consistence of lard. Thorium compounds have also been obtained with phenol, 2 : 4 : 6-tribromophenol, *p*-cresol, resorcinol, pyrogallol, α - and β -naphthols, gallic acid, and tannic acid. The *phthalate* and *camphorate* are sparingly soluble in water, whilst the other derivatives are insoluble. All these compounds are amorphous substances to which no very definite formula can be assigned.

Thorium lactate, $(\text{OH}\cdot\text{CHMe}\cdot\text{CO}_2)_4\text{Th}\cdot 2\text{H}_2\text{O}$, forms opaque, white, tabular, deliquescent crystals. The *benzenesulphonate*, $(\text{C}_6\text{H}_5\cdot\text{SO}_3)_4\text{Th}$, forms small, colourless crystals. The *naphthalene- α -sulphonate*, $(\text{C}_{10}\text{H}_7\cdot\text{SO}_3)_4\text{Th}$, and the corresponding *naphthalene- β -sulphonate* are soluble in water. The *phenol-p-sulphonate* (sulphocarbolate),



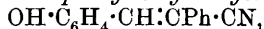
crystallises in pale pink, transparent prisms and is much more radio-active than the insoluble oleate obtained by precipitation (compare Rutherford and Soddy, *Trans.*, 1902, 81, 321, 837). The *β -naphthol-6-sulphonate*, $(\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3)_4\text{Th}\cdot 9\text{H}_2\text{O}$, forms colourless crystals. The *camphorsulphonate*, $(\text{C}_{10}\text{H}_{15}\text{O}\cdot\text{SO}_3)_4\text{Th}\cdot 9\text{H}_2\text{O}$, crystallises from water in colourless, transparent, lustrous prisms.

E. G.

Mechanism of the Transformation of β -Unsaturated α -Hydroxy-acids into the Isomeric γ -Ketonic Acids. EMIL ERLÉNMEYER, jun. (*Ber.*, 1904, 37, 3124—3128. Compare *Abstr.*, 1903, i, 676).—Largely a theoretical paper. It is shown that the first product of the transformation of phenyl- α -hydroxycrotonic acid under the influence of acetic anhydride containing a few drops of sulphuric

acid is Δ^{β} -phenylcrotonolactone, and this fact is considered to prove that the first step in the transformation of $\beta\gamma$ -unsaturated α -hydroxy-acids is the wandering of the α -hydroxyl group according to the scheme: $\text{CHPh}\cdot\text{CR}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H} \rightarrow \text{OH}\cdot\text{CHPh}\cdot\text{CR}\cdot\text{CH}\cdot\text{CO}_2\text{H}$.
W. A. D.

α -Phenyl-*o*-hydroxycinnamionitrile and α -Phenylcoumarin. WALTHER BORSCHÉ and F. STREITBERGER (*Ber.*, 1904, 37, 3163—3167).—Salicylaldehyde and benzyl cyanide condense in the presence of sodium hydroxide to form α -phenyl-*o*-hydroxycinnamionitrile,



which separates from aqueous methyl alcohol in yellow needles and melts at 104° . When boiled with dilute hydrochloric acid, it is converted into 3-phenylcoumarin, $\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CPh}\cdot\text{CO}$, which separates in needles and melts at 140° . By the action of concentrated sodium ethoxide solution, 3-phenylcoumarin is converted into α -phenylcoumarinic acid, which did not undergo transformation into the isomeric α -phenylcoumaric acid. α -Phenyl-*o*-hydroxycinnamionitrile could not be converted into 2-hydroxy-3-phenylquinoline.
A. McK.

Derivatives of α - and β -Naphthisatins. CAMILLE DREYFUS and HENRY DREYFUS (D.R.-P. 153418. Compare this vol., i, 832).—The method employed for the preparation of naphthalides of naphthisatin may also be employed to prepare the corresponding anilides and toluidides. The hydrocyanocarbo-diarylimides are prepared from the corresponding thiocarbamides, and probably have the constitution $\text{R}^{\text{II}}\cdot\text{CR}^{\text{I}}\cdot\text{CN}$, where R^{I} is the residue of α - or β -naphthylamine, and R^{II} is the residue of β -naphthylamine, aniline, *o*-toluidine, or *p*-toluidine.

Hydrocyanocarbo- β -naphthylphenylimide melts at 146° ; *hydrocyanocarbo- β -naphthyl-*o*-tolylimide* at 106° ; *hydrocyanocarbo- β -naphthyl-*p*-tolylimide* at 129° ; *hydrocyanocarbo- β -naphthyl- α -naphthylimide* at 165° ; *hydrocyanocarbo- α -naphthylphenylimide* at 121° ; *hydrocyanocarbo- α -naphthyl-*o*-tolylimide* at 97° , and *hydrocyanocarbo- α -naphthyl-*p*-tolylimide* at 151° .

Warm sulphuric acid converts these compounds into the corresponding isatin derivatives, acid amides being formed as intermediate products. Alkali sulphides reduce the isatin derivatives to naphthaleneindigotin compounds.
C. H. D.

Preparation of Indoxylic Acid and Indoxyl. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 152548).—In the preparation of indoxylic acid and indoxyl from salts of phenylglycine-*o*-carboxylic acid, the salt is intimately mixed with the alkali hydroxide in the dry state. If mixed in aqueous solution and evaporated before fusion, the yield is reduced to 25—30 per cent. A yield of 90 per cent. is, however, obtained if the evaporation is performed in a vacuum, the temperature being gradually raised to 180 — 200° , when the reaction sets in.

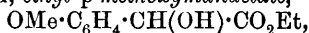
C. H. D.

Bromination of Indigotin. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 151866. Compare this vol., i, 57, 167, 587).—In the bromination of indigotin in the presence of water, bromoisatin is produced (this vol., i, 500). This is avoided when the indigotin is made into a paste with 78 per cent. sulphuric acid, that is, of such strength that indigotin sulphate, but no sulphonated derivative, is formed, and bromine is then added. The proportion of bromine in the products, which resemble those obtained by dry bromination, may be varied.

C. H. D.

Optically Active *p*-Methoxymandelic Acids. EDUARD KNORR (*Ber.*, 1904, 37, 3172—3176).—Ostwald has shown that the electrical conductivity of anisic acid is only slightly less than that of benzoic acid, whilst Baeyer and Villiger (*Abstr.*, 1902, i, 770) observed that the basic character of triphenylcarbinol is enormously increased by the introduction of methoxyl groupings. The author has accordingly investigated the effect on the optical activity of mandelic acid by the methoxylation of this acid in the *p*-position.

Anisaldehyde cyanohydrin crystallises in prisms and melts at 66—67°. When its imino-ether hydrochloride, prepared by the action of dry hydrogen chloride on a mixture of the cyanohydrin and ethyl alcohol, is hydrolysed, *ethyl p-methoxymandelate*,



is formed; this separates from water or from light petroleum in needles and melts at 47—48°.

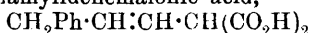
p-Methoxymandelamide, obtained as a by-product, separates from ethyl alcohol in silky leaflets and melts at 163—164°. *r-p*-Methoxymandelic acid, obtained by hydrolysis either of the ethyl ester or of the amide, crystallises in leaflets and melts at 108—109°. When the crop obtained by neutralising it with cinchonine is repeatedly crystallised from water, cinchonine *d-p*-methoxymandelate is obtained. The separation of *r-p*-methoxymandelic acid into its optically active components is conveniently attained on the larger scale by aid of a nucleus of the cinchonine *d*-salt, according to the method used by Lewkowitsch, Rimbach, and McKenzie for the preparation of *d*-mandelic acid.

One hundred c.c. of water dissolve, at 10°, 0.506 gram of the cinchonine *d*-salt (m. p. 160°) and 0.637 gram of the cinchonine *l*-salt (m. p. about 174—175°), *d*- and *l-p*-Methoxymandelic acids separate from water in monoclinic, sphenoidal crystals melting at 104—105° and contain 2H₂O. The crystals were measured. The *d*-acid gives $[\alpha]_D + 146.14^\circ$ at 19° (sp. gr. = 1.0047), and the *l*-acid $[\alpha]_D - 145.24^\circ$ at 16° (sp. gr. = 1.0053), the solvent being water in each case. The introduction of the methoxyl grouping in the *p*-position into mandelic acid accordingly lowers the specific rotation of the latter by about 10°.

The inactive *p*-methoxymandelic acid is racemic, and not a *dl*-mixture, since its crystalline form is different from that of the active isomerides.

A. McK.

The Two Isomeric Hydrocinnamylidenemalonic Acids. C. N. RIIBER (*Ber.*, 1904, 37, 3120—3124).—Thiele and Meisenheimer's $\alpha\delta$ -hydrocinnamylidenemalonic acid,



(Abstr., 1899, i, 603), is shown to have the structure attributed to it; the oxidation of its methyl ester giving phenylacetic acid, malonic acid, and carbon dioxide. *Methyl $\alpha\delta$ -hydrocinnamylidenemalonate*, $\text{CH}_2\text{Ph}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}(\text{COMe})_2$, boils at 123° under 0.16 mm. and at 187° under 12 mm. pressure, undergoing in the latter case considerable decomposition.

$\alpha\delta$ -Hydrocinnamylidenemalonic acid, when kept in a closed tube, gradually changes into the $\gamma\delta$ -isomeric, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{C}(\text{CO}_2\text{H})_2$; in presence of concentrated hydrochloric acid, the change is complete in about a month. The product crystallises from benzene in small bundles of needles and melts at 124° ; its structure follows from its giving hydrocinnamic and oxalic acids on oxidation with alkaline potassium permanganate. W. A. D.

Phthalyl Derivatives of α -Aminopropionic Acid. RUDOLF ANDREASCH (*Monatsh.*, 1904, 25, 774—784).—*Ethyl phthalyl- α -aminopropionate*, $\text{C}_6\text{H}_4\cdot(\text{CO})_2\cdot\text{N}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$, formed by the action of potassium phthalimide on ethyl α -bromopropionate at 140° , crystallises from carbon disulphide in large plates, from alcohol in thick needles, and melts at 65° . When heated with dilute sulphuric acid at 120° , the ester is hydrolysed to phthalic acid, alanine, and ethyl alcohol; the action of chlorosulphonic acid leads to the same hydrolysis, but with decomposition of the alanine.

Phthalylalanine, $\text{C}_6\text{H}_4\cdot(\text{CO})_2\cdot\text{N}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, is formed by heating phthalic anhydride with alanine at 160 — 170° . It crystallises in sheaves of needles, melts at 164° , and is soluble in boiling water, alcohol, acetone, or ether. The *phenyl* ester, obtained when phthalylalanine is heated with phenol and phosphorus oxychloride, crystallises in small needles and melts at 99° .

Phthaloylalanine, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}\cdot\text{H}_2\text{O}$, is obtained by boiling ethyl phthalyl- α -aminopropionate with baryta in aqueous solution or by warming phthalylalanine with aqueous potassium hydroxide. The acid crystallises from warm water, melts at 129° , is soluble in alcohol, ether, or glacial acetic acid, is hydrolysed to phthalic acid and alanine on prolonged warming with water, and yields phthalylalanine when dried at high temperatures. The action of potassium phthalimide on ethyl $\alpha\beta$ -dibromopropionate leads to the formation of an oil, $\text{C}_5\text{H}_7\text{O}_2\text{Br}$, which has a suffocating odour and is probably a condensation product of ethyl bromoacrylate. G. Y.

Benzylphthalimide and Benzylisophthalimide. F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 7, 77—82).—The paper contains crystallographic measurements of these two compounds and of a second form of benzylphthalimide obtained on one occasion from benzene solution. This form is designated as the β -compound, and passes before fusion into the more stable α -compound, melting at 115.5° .

α -Benzylphthalimide is triclinic-pinacoidal [$a:b:c=0.8443:1:1.3600$; $\alpha=108^\circ24'$; $\beta=120^\circ7'$; $\gamma=73^\circ8'$]; β -benzylphthalimide, monoclinic-prismatic, [$a:b:c=0.8476:1:0.5092$; $\beta=70^\circ42'$]; benzylphthalisoimide, monoclinic-prismatic [$a:b:c=1.2303:1:0.5932$; $\beta=71^\circ46'$]. Attention

is drawn to the similarity of the ratio $a:b$ with the two forms of the first compound and to the similarity of the ratio $b:c$ with the β -modification and the isomeric *isoimide*. The author has observed similar relationships in the ratio $a:b$ with the red α - and the less stable yellow β -forms of 3:4-dinitrodiethylaniline.

The α - and β -benzylphthalimides are probably desmotropically related. G. D. L.

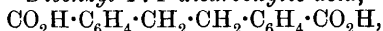
Action of Persulphates on Aromatic Nitriles. PAUL KATTWINKEL and RICHARD WOLFFENSTEIN (*Ber.*, 1904, 37, 3221—3227. Compare Abstr., 1901, i, 594).—*Terephthalicmonothiamide*,



formed by the action of hydrogen sulphide on cyanobenzoic acid, melts at 247° ; *terephthalhydroxamide*, $\text{NH}_2\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, is not melted at 320° .

Terephthalamic acid is not melted on heating to 300° , but sublimes about 250° ; it forms a colourless, amorphous *silver salt*, a *methyl ester* melting at 201° , and is converted on boiling with alkali into *terephthalic acid*. *o-Toluamide* crystallises in glistening needles melting at 147° , *m-toluamide* in rhombic prisms which melt at 97° . When acted on with potassium persulphate, *p-toluenitrile* yields *p-cyanobenzoic acid*, *p-dibenzylidinitrile*, and an amorphous, brown powder with a molecular weight of about 1200; whilst when oxidised with permanganate or chromic acid respectively, *terephthalamic acid* and *p-toluic acid* are the chief products. E. F. A.

The Condensing Influence of Potassium Persulphate on the Toluic Acids. CARL FISCHER and RICHARD WOLFFENSTEIN (*Ber.*, 1904, 37, 3215—3220).—*Dibenzyl-4:4'-dicarboxylic acid*,



formed by the action of potassium persulphate on *p-toluic acid*, is a colourless, amorphous substance which is not melted at 320° ; the *methyl ester* melts at 119° , the *ethyl ester* separates from alcohol in bright yellow needles melting at 100° , the *chloride* forms plates and cubes melting at 119° . *Dibenzyl-2:2'-dicarboxylic acid*, prepared in the same way from *o-toluic acid*, melts at 231° and is identical with the acid described by Graebe (*Ber.*, 1875, 8, 1055) and Dobreff (*Annalen*, 1887, 239, 67). E. F. A.

Action of Eosin Solution on Oxidisable Substances. WALTHER STRAUB (*Chem. Centr.*, 1904, ii, 655; from *Arch. exp. Path. Pharm.*, 51, 383—390).—Iodine is liberated from a solution of potassium iodide in the presence of eosin and oxygen in the light. This reaction also occurs in the dark, but very slowly. In strong solutions of the iodide, the amount of iodine set free is proportional to the amount of eosin and the length of time. In very dilute solutions, the same amount of eosin liberates the more iodine in the same time, the more the eosin is diluted. This is explained by the fact that in dilute solutions the active rays, which give a green fluorescence, can penetrate the whole fluid, whilst in concentrated solutions they are absorbed at the surface. For the complete discharge of colour from eosin, 65

molecules of oxygen are required per molecule of eosin. The reaction probably depends on the formation of eosin peroxide. W. D. H.

Substances contained in "Orchil" Lichens. RONCERAY (*Bull. Soc. chim.*, 1904, [iii], 31, 1097—1103. Compare Juillard, this vol., i, 593).—Erythrin (erythric acid) was isolated from *Roccella Montagnei* (compare Hesse, Abstr., 1898, 531, 679) and *Dendrographa leucophæa*; lecanoric acid was obtained from *Roccella tinctoria*; whilst orcinol was found in all three lichens. Lecanoric acid was isolated by extracting the plant with warm alcohol (95°), converting the crude acid into the calcium salt, and crystallising the regenerated acid from alcohol. It melted at 201° on the Maquenne block. Erythrin was obtained by extracting the plants with dilute acetic acid (20 per cent.) and crystallising from alcohol by addition of chloroform; it melted at 164° on the Maquenne block (compare Juillard and Hesse, *loc. cit.*). T. A. H.

Gattermann's Reaction for the Synthesis of Aromatic Aldehydes. Application to *p*-Xylene. CURIO M. MUNDICI (*Gazzetta*, 1904, 34, ii, 114—124).—Francesconi and the author (Abstr., 1903, i, 426) have shown that when *p*-xylene is used in Gattermann's reaction for the synthesis of aromatic aldehydes, intermolecular change occurs, 2:4-dimethylbenzaldehyde being formed.

In order to confirm this result, which is at variance with the work of Harding and Cohen (Abstr., 1901, i, 725), the author has prepared dimethylcinnamic acids: (1) from 2:5-dimethylbenzaldehyde prepared by Bouveault's method (Abstr., 1896, i, 649, and 1897, i, 530); (2) from *m*-xylene, and (3) from *p*-xylene, both by Gattermann's synthesis. The dimethylcinnamic acids obtained by the last two methods are identical, and different from that yielded by the first method.

Hence, in the action of the hypothetical formyl chloride in the nascent condition on *p*-xylene, one methyl group is displaced from the para- to the meta-position with regard to the other, whilst the aldehyde group assumes the place left vacant by the displacement of the methyl.

That this displacement is due to the influence of the aluminium chloride employed is shown by the fact that when this condensing agent is allowed to act under conditions similar to those prevailing in Gattermann's synthesis, on *p*-xylene, part of the latter is transformed into *m*-xylene. T. H. P.

A Third Modification of Aldoximes. ERNST BECKMANN (*Ber.*, 1904, 37, 3042—3044).—*anti*Anisaldoxime exists both as platelets melting at 45° and needles melting at 64°; these can be mutually converted into one another. *anti*Benzaldoxime, when crystallised from water, melts at 16°; a modification melting at 5° is obtained on rubbing the strongly cooled, melted aldoxime. Cuminaldoxime, when crystallised from light petroleum, melts at 61°; when crystallised from water, it melts at 48°, whilst a third crystalline form melts at 35°. The author, for the moment, regards these modifications as monotropic.

E. F. A.

Halogen-nitro- and Nitroamino-benzophenones. FRANZ KUNC-KELL [and L. SZULC] (*Ber.*, 1904, **37**, 3484—3486. Compare Consonno, this vol., i, 676).—3:3'-*Dibromodinitrobenzophenone*, $C_{13}H_6O_5N_2Br_2$, prepared by heating *m*-dibromobenzophenone with fuming nitric acid, separates from benzene in pale yellow crystals and melts at 209°. Alcoholic ammonia converts it at 130° into 3-bromo-3'-aminodinitrobenzophenone, $C_{13}H_8O_5N_3Br$, crystallising from alcohol in yellow, glistening leaflets and melting at 250°. Piperidine reacts with 3:3'-dibromodinitrobenzophenone at 125°, forming 3:3'-*dipiperidinodinitrobenzophenone*, $C_{23}H_{26}O_5N_4$, which crystallises from alcohol in yellow needles or from acetic acid in leaflets and melts at 190°.

4:3'-*Dibromobenzophenone*, $C_{13}H_8OBr_2$, prepared by heating *p*-bromobenzophenone with bromine and water at 160°, melts at 130° and reacts with fuming nitric acid to form 4:3'-*dibromodinitrobenzophenone*, $C_{13}H_6O_5N_2Br_2$, separating from benzene and acetic acid in yellow crystals and melting at 181°. Alcoholic ammonia converts it at 130° into 3-bromo-4-aminodinitrobenzophenone, $C_{13}H_8O_5N_3Br$, crystallising from alcohol in small, yellow needles and melting at 240°. The same compound is obtained from 4-chloro-3'-bromodinitrobenzophenone.

3'-*Bromo-4-piperidinodinitrobenzophenone*, $C_{18}H_{16}O_5N_3Br$, crystallises from alcohol in yellowish-red needles, melts and decomposes at 76°, and dissolves in alcohol or chloroform. C. H. D.

Dibenzylideneacetone and Triphenylmethane. ADOLF BAEYER and VICTOR VILLIGER [and, in part, HENRY BASSETT, jun.] (*Ber.*, 1904, **37**, 3191—3215. Compare *Abstr.*, 1902, i, 380, 769; 1903, i, 811; 1904, i, 308).—*o*-Aminotriphenylcarbinol, prepared by the interaction of methyl anthranilate and magnesium phenyl bromide, crystallises in colourless plates from ether and melts at 121.5°. Only colourless salts have been obtained, although the momentary existence of coloured salts is indicated by the very fugitive blue colour of the hydrochloride of the carbinyl chloride when brought into contact with water. The *hydrochloride* crystallises in colourless, prismatic needles, which on heating become brown at 140° and melt and decompose at 164°; the *hydrochloride* of the carbinyl chloride, $C_{19}H_{17}NCl_2$, crystallises in short, transparent, rectangular prisms. The *picrate* separates from benzene in bright, yellow, rhombic plates, melting and decomposing at 122.5—123.5°, whilst the dichloride, on heating with pyridine, forms *anhydro-o-aminotriphenylcarbinol*, $(C_{19}H_{15}N)_2$, which crystallises in colourless prisms, sparingly soluble in neutral solvents and melting and decomposing at 250°; its *acetate* crystallises in large prisms melting at 134.5—137° and is converted by dilute acids into *acetyl-o-aminotriphenylcarbinol*, which melts at 192°.

o-Aminotriphenylmethane, obtained by reducing the carbinol with zinc dust and acetic acid, crystallises from ether in plates melting at 128—130° or from benzene in octahedra, which contain a molecule of the solvent and melt at 94—95°; the *acetyl* derivative forms thick, colourless prisms melting at 154—155°; the *benzoyl* compound melts at 94—95°, the *hydrochloride* crystallises in many-faced prisms, the *sulphate* in needles, the *oxalate* in platelets, and the *nitrate* in very slender needles.

Methyl phenylanthranilate, an odourless, viscid, colourless oil, boiling at $216.5\text{--}217.5^\circ$ under 18.5 mm. pressure, interacts with magnesium phenyl bromide to form *o*-phenylaminotriphenylcarbinol, which crystallises in colourless prisms melting at $127.5\text{--}128.5^\circ$ and forms an *anhydride*, *5:5-diphenylhydroacridine*, $\text{C}_{25}\text{H}_{19}\text{N}$, melting at $243.5\text{--}244.5^\circ$, and forming an *acetate* melting at $216.5\text{--}218.5^\circ$.

o-Dimethylaminotriphenylcarbinol crystallises from light petroleum or alcohol in short, colourless, flat prisms melting at $156\text{--}160^\circ$. The *dichloride*, which has only been obtained as a syrup, shows a well-marked, but fugitive, blue-violet coloration when brought into contact with water, the *hydrochloride* forms large prisms containing a molecule of water, melting at $149\text{--}157^\circ$ or when anhydrous at 187° ; the *picrate*, which crystallises in sparingly soluble yellow rhombs, being specially characteristic.

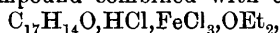
o-Methylaminotriphenylmethane, formed by the action of hydrogen chloride on dimethylaminotriphenylcarbinol, crystallises from benzene in rhombohedra melting at $130\text{--}132^\circ$ and forms an *acetate* melting at $147.5\text{--}148.5^\circ$; the *hydrochloride* forms prisms, which soften at 190° and melt and decompose at 210° , the *sulphate* crystallises in needles, the *oxalate* in rhombic plates, and the *nitrate* in aggregates of needles.

The reactions of *o*-aminotriphenylcarbinol resemble those of the para-compound as regards the formation of a salt and also those of a bimolecular carbinol anhydride. E. F. A.

Additive Compounds of Dibenzylideneacetone and Hydrogen Chloride. FRITZ STRAUS (*Ber.*, 1904, **37**, 3277—3293. Compare Baeyer, *Abstr.*, 1902, i, 380, 769; Vorländer, 1903, i, 496; Thiele and Straus, *ibid.*, i, 707).—Dibenzylideneacetone, in dry ethereal solution, is capable of forming definite compounds with certain metallic salts. With mercuric chloride, the compound $\text{C}_{17}\text{H}_{14}\text{O}, \text{HgCl}_2, \text{OEt}_2, \text{HgCl}_2$ is obtained. It crystallises in dark yellow, strongly refractive prisms, begins to sinter at $115\text{--}120^\circ$, and rapidly decomposes at 185° . The ether is firmly united; even when left for several days in a vacuum the crystals remain clear. Sodium chloride solution or chloroform decomposes them. When left in contact with dry hydrogen chloride, it forms the orange-coloured compound,

$\text{C}_{17}\text{H}_{14}\text{O}, \text{HgCl}_2, \text{OEt}_2, \text{HgCl}_2, \text{HCl}$, which melts at 129° . A compound, $\text{C}_{17}\text{H}_{14}\text{O}, \text{HCl}, \text{HgCl}_2$, is formed when a dry ethereal solution of hydrogen chloride is added to an ethereal solution of the ketone and mercuric chloride. It separates in the form of voluminous, orange-coloured crystals which gradually become transformed into compact needles. It sinters at $125\text{--}128^\circ$ and melts sharply at 134° to a dark liquid and is not decomposed by chloroform or benzene.

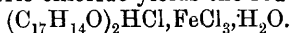
The compound $\text{C}_{17}\text{H}_{14}\text{O}, \text{FeCl}_3$ crystallises in brown needles with a brilliant green lustre, melts at 163° , and is decomposed by alcohol, but not by hot chloroform. Dry hydrogen chloride converts it into the compound $\text{C}_{17}\text{H}_{14}\text{O}, \text{HCl}, \text{FeCl}_3$, which has a carmine-red colour. The same compound combined with ether,



is obtained when a solution of hydrogen chloride and ferric chloride in dry ether is added to the red benzylideneacetone dihydrochloride.

A compound $(C_{17}H_{14}O)_2 \cdot H_2PtCl_6 \cdot OEt_2$ has been obtained by a similar method; it crystallises in carmine-red, glistening prisms. A second compound with $2Et_2O$ has also been obtained. Dibenzylideneacetone in ethereal solution reacts with fuming hydrochloric acid yielding a compound $C_{17}H_{14}O \cdot HCl$, which crystallises in yellow needles. On exposure to the air, it rapidly decomposes into its components, and on mixing with an ethereal solution of hydrogen chloride or with the dry gas it yields the red dihydrochloride.

A solution of chloroplatinic acid transforms the yellow hydrochloride into the compound $(C_{17}H_{14}O)_2 \cdot H_2PtCl_6 \cdot 2H_2O$, which crystallises in brick-red needles; ferric chloride yields the red compound,



When an ethereal solution of the colourless hydrochloride (Abstr., 1903, i, 707) is shaken with water, the aqueous solution gives a neutral reaction, but on the addition of nitric acid and silver nitrate gives a minute amount of precipitate. The addition of an ethereal solution of hydrogen chloride to a colourless solution of this hydrochloride in ether produces an intense yellow coloration and the product formed yields, on addition of bromine in chloroform solution, a certain amount of dibenzylideneacetone tetrabromide. There is thus probably equilibrium between the systems: colourless hydrochloride \rightleftharpoons ketone and hydrogen chloride \rightleftharpoons yellow labile hydrochloride (decomposed by water). The addition of ethereal solutions of ferric chloride or mercuric chloride to ethereal solutions of the colourless hydrochloride produces crystalline precipitates of the compounds described above, for instance, $C_{17}H_{14}O \cdot HCl \cdot HgCl_2$.

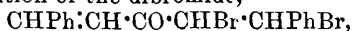
J. J. S.

Addition of Acids to $\alpha\beta$ -Unsaturated Ketones. DANIEL VORLÄNDER and CARL SIEBERT (*Ber.*, 1904, 37, 3364—3370. Compare Abstr., 1903, i, 495, 496; this vol., i, 65, 450, 535, 659).—Two pairs of additive isomeric hydrobromides of dibenzylideneacetone are known, two isomeric monohydrobromides, A and B, and two isomeric dihydrobromides, 2A and 2B.

Dibenzylideneacetone dihydrobromide, 2B, prepared by passing dry hydrogen bromide over dibenzylacetone for 16—20 hours, separates from a mixture of light petroleum and amyl alcohol in tetragonal plates. At the ordinary temperature, it gradually becomes brown, and sometimes hydrogen bromide is evolved from it. By the action of sodium ethoxide, it is converted into *dibenzylideneacetone hydrobromide*, B, which separates from a mixture of light petroleum and amyl alcohol in glistening leaflets, which become yellow at 75°, orange at 90°, and melt at 119—121° to a reddish-brown liquid. On being kept in a desiccator it gradually becomes brown, but is more stable than the dihydrobromide. Dry hydrogen bromide very readily converts it into the di-compound.

When hydrogen bromide is passed into a benzene solution of the hydrobromides B or 2B at 0°, a mixture of dibenzylideneacetone and the hydrobromide B is produced.

By the action of bromine on the hydrobromides B and 2B, either the tetrabromide melting above 200° or *tribromodibenzylacetone* having the probable composition $\text{CHPhBr}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CHBr}\cdot\text{CHPhBr}$ is formed, according to the amount of bromine used. The latter separates from alcohol in white needles, which become yellow at about 125° and melt at $134\text{--}137^{\circ}$; it may also be obtained by passing dry hydrogen bromide into a solution of the dibromide,



in glacial acetic acid.

Dibenzylideneacetone is coloured orange by bromine vapour, whilst its hydrobromide A becomes red. Bromine vapour causes dianisylideneacetone to become reddish-violet, anisylideneacetophenone brown, anisylidenebenzylideneacetone violet-red to brown, dibenzylidene-cyclopentanone reddish-orange, and difurfurylidene-cyclopentanone black. These colorations are not caused by hydrogen haloids.

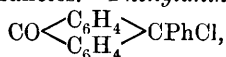
A. McK.

Benzopinacone and Benzopinacolin. AMAND VALEUR (*Compt. rend.*, 1904, 139, 480—481).—The product of the reaction of methyl or ethyl oxalate on magnesium phenyl bromide is benzopinacone (compare Abstr., 1903, i, 416), and not β -benzopinacolin, as stated by Dilthey and Last (compare this vol., i, 667).

M. A. W.

Alkyloxyanthranoles. CARL LIEBERMANN, A. GLAWE, and SIMON LINDENBAUM (*Ber.*, 1904, 37, 3337—3343).—The study of alkyloxyanthranoles begun by Liebermann has been extended.

Alkyloxyanthranoles were formerly converted into their chlorides by means of phosphorus pentachloride; the chlorides are easily prepared by passing hydrogen chloride into chloroform or benzene solutions of alkyloxyanthranoles. *Phenylanthrone chloride*,



crystallises in needles and melts at $168\text{--}169^{\circ}$. *Phenylanthrone bromide* forms needles melting at $145\text{--}147^{\circ}$. *Phenylanthrone-p-toluidide*, $\text{C}_{14}\text{H}_8\text{OPh}\cdot\text{NH}\cdot\text{C}_7\text{H}_7$, prepared from phenylanthrone chloride and *p*-toluidine, forms yellow needles and melts and decomposes at $174\text{--}178^{\circ}$.

Alkylanthrone chlorides act on metals. When benzene solutions of ethyl-, isobutyl-, and isoamyl-anthrone chlorides respectively are left in contact with zinc turnings in an atmosphere of carbon dioxide, they gradually assume a yellow colour, which disappears in the presence of air.

When a benzene solution of phenylanthrone chloride is shaken with mercury for several days, a current of dry oxygen being passed through the liquid during this time, a product free from chlorine is obtained; this melts at 219° and is probably the peroxide, $(\text{C}_{20}\text{H}_{13}\text{O}_2)_2$. When a benzene or chloroform solution of phenylanthrone is treated with hydrogen iodide, crystals of *phenylanthranole periodide hydriodide*, $(\text{C}_{20}\text{H}_{14}\text{O}, \text{HI})_2\text{I}_3$, are obtained; this forms a brown solution with glacial acetic acid or acetone, and the addition of water causes the separation of phenylanthranole.

Other iodine compounds of the anthraquinone series are described. When hydrogen iodide is passed into a benzene solution of anthraquinone, dark crystals, like those of iodine, separate. *Anthranole diiodide*, $C_{14}H_{10}OI_2$, prepared by mixing concentrated benzene solutions of anthranole and iodine, forms dark leaflets. Chrysazin forms dark crystals with hydriodic acid. Quinazarin, anthrarufin, and alizarin also form compounds with hydriodic acid. A. McK.

Chloro-1:7-dihydroxyanthraquinone. R. WEDEKIND & Co. (D.R.-P. 153194. Compare this vol., i, 813).—1:7-Dihydroxyanthraquinone resembles the β -hydroxyanthraquinones in being able to take up chlorine in alkaline solution. Not more than one atom of chlorine can be introduced in this way, although two atoms are taken up by the β -hydroxyanthraquinones. The chlorine atom enters a β -position. *Chloro-1:7-dihydroxyanthraquinone* dissolves very readily in hot alcohol or acetic acid, readily in ether, sparingly in benzene. It melts and decomposes on heating, hydrogen chloride being evolved.

C. H. D.

[**Sulphonic Acids of *p*-Diaminoanthrarufin Dialkyl Ether.**] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 152013).—Alkali sulphites convert the dinitro-derivatives of dihydroxyanthraquinone alkyl ethers, especially the alkyl ethers of *p*-dinitroanthrarufin, into ethers of diaminosulphonic acids. The alkyl ethers of *p*-diaminoanthrarufinsulphonic acid are violet dyes, and are readily hydrolysed, yielding *p*-diaminoanthrarufinsulphonic acid. C. H. D.

“**Exodin.**” F. ZERNIK (*Chem. Centr.*, 1904, ii, 709; from *Apoth.-Zeit.*, 19, 598—600).—“Exodin” (this vol., i, 809) is not the tetramethyl ether of diacetylrufigallic acid, but a mixture of the hexamethyl ether of rufigallic acid, the pentamethyl ether of acetylrufigallic acid, and the tetramethyl ether of diacetylrufigallic acid. The physiological action is due to the presence of the first-named compound, the other two components being inactive. The hexamethyl ether of rufigallic acid, $C_{20}H_{20}O_8$, prepared from the residue after extracting commercial “exodin” tablets with chloroform, evaporating, crystallising from benzene, and hydrolysing with alcoholic potash, crystallises from ethyl acetate in pale yellow needles and melts at 245° ; it is not attacked by an aqueous or a cold alcoholic solution of potassium hydroxide, and does not give Bornträger’s aloin reaction, but forms a purple-violet coloration with concentrated sulphuric acid. The tetramethyl ether, $C_{18}H_{16}O_8$, and the pentamethyl ether of rufigallic acid may be isolated from the mother liquor of the hexamethyl ether. The former crystallises from ethyl acetate or chloroform in yellow, prismatic leaflets and melts at 235 — 237° ; it dissolves in a large quantity of aqueous potassium hydroxide solution, forming a blood-red solution, and with concentrated sulphuric acid it gives a purple-violet coloration. The pentamethyl ether, $C_{19}H_{18}O_8$, crystallises from ethyl acetate or boiling alcohol in yellow needles and melts at 192 — 194° ; it dissolves in concentrated sulphuric acid forming a purple-red solution, and with aqueous potassium hydroxide solution gives a dark-red coloration without appreciably dissolving. This compound was found to be

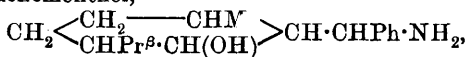
identical with Klobukowski's tetramethyl ether of rufigallic acid (Abstr., 1877, ii, 618). The *methyl ether* of diacetylrufigallic acid, $C_{22}H_{20}O_{10}$, crystallises from ethyl acetate in yellow leaflets and melts and decomposes at 262° ; it is very sparingly soluble in alcohol or ether, more soluble in benzene, ethyl acetate, or glacial acetic acid, and very readily so in chloroform. It is not attacked by a cold aqueous solution of potassium hydroxide, but dissolves in concentrated sulphuric acid forming a purple violet solution. The *pentamethyl ether* of acetylrufigallic acid, $C_{21}H_{20}O_9$, forms yellow leaflets, which begin to melt about $179-180^{\circ}$ but become completely liquid only about 209° . This compound is somewhat more readily soluble in ethyl acetate than the preceding substance, but resembles it in other properties. The tetramethyl and pentamethyl ethers of rufigallic acid with their acetyl derivatives give Bornträger's aloin reaction. E. W. W.

Condensation of Cochenillic Acid with Succinic Acid.

CARL LIEBERMANN and HUGO VOSWINCKEL (*Ber.*, 1904, 37, 3344—3348).—*Cochenillic anhydride* is obtained by boiling a mixture of cochenillic acid, acetyl chloride, and phosphorus oxychloride, when the *acetic acid* derivative is formed; this separates from glacial acetic acid in prisms and forms the anhydride when heated at 115° . When cochenillic anhydride is fused with a mixture of succinic acid and succinic anhydride at $200-205^{\circ}$, *dihydroxydimethylethinediphtalide*, $CO \langle \underset{\text{O}}{\text{C}_6\text{H}_2\text{Me}(\text{OH})} \rangle \text{C}:\text{CH}:\text{CH}:\text{C} \langle \underset{\text{O}}{\text{C}_6\text{H}_2\text{Me}(\text{OH})} \rangle \text{CO}$, is produced as a yellow, crystalline mass, which may be heated to 330° without its melting; it forms a yellow solution with concentrated sulphuric acid. When cochenillic anhydride is fused with succinic anhydride at about 160° , dihydroxydimethylethinediphtalidedicarboxylic acid is formed in small amount.

Dihydroxydimethylisoethinediphtalide (*tetrahydroxydimethylnaphthacenequinone*), $\text{OH} \cdot \text{C} \langle \begin{array}{c} \text{CH}:\text{CMe}:\text{C}(\text{OH}):\text{C}:\text{CO}:\text{C} \\ \text{CH} \text{---} \text{C}:\text{C}(\text{OH}):\text{C}:\text{CO}:\text{C} \end{array} \text{---} \text{CH} \rangle \text{C} \cdot \text{OH}$, prepared by heating dihydroxydimethylethinediphtalide with sodium methoxide at $140-145^{\circ}$, crystallises in red needles, which may be heated to 330° without melting; its alcoholic solution exhibits orange fluorescence. Sodium chloride precipitates it from its alkaline solution, which is cochineal-red in colour. A. McK.

Menthones. CAMILLE MARTINE (*Ann. Chim. Phys.*, 1904, [viii], 3, 49—144).—In addition to a full account of work already published (compare Abstr., 1901, i, 559; 1902, i, 629; 1903, i, 315), this paper contains the following corrections and additions: the benzylidenementhone, melting at 51° , crystallises in the monoclinic system [$a:b:c=1.3285:1:1.2749$; $\beta=95^{\circ}34'$]; the compounds described as oximes of the benzylidenementhones are hydroxylamine derivatives, $\text{CH}_2 \langle \begin{array}{c} \text{CH}_2 \cdot \text{CHMe} \\ \text{CHPr}^{\beta} \text{---} \text{CO} \end{array} \rangle \text{CH} \cdot \text{CHPh} \cdot \text{NH} \cdot \text{OH}$, yielding, on reduction, hydroaminobenzylidenementhol,



boiling at 205—208° under 15 mm. pressure; by using Haller's method for the preparation of sodiomenthol (compare this vol., i, 600), a slightly better yield of benzylidenementhone is obtained than by the original method, and the following derivatives were similarly prepared: methylmenthone, obtained by the action of methyl iodide on sodiomenthone, is a colourless liquid with an odour like that of camphor, boils at 96—97° under 13 mm. pressure, has a sp. gr. 0.9173 at 18°/18° and $[\alpha]_D + 44^\circ 15'$, and gives a *semicarbazone* melting at 203—204°; ethylmenthone, similarly prepared, boils at 106—108° under 15 mm. pressure, has a sp. gr. 0.9208 at 18°/18° and $[\alpha]_D + 82^\circ 32'$; *anisylidene-menthone*, prepared by the action of anisaldehyde on sodiomenthone, forms colourless crystals melting at 115—116°, has $[\alpha]_D - 278^\circ 26'$, and forms a *hydroxylamine* derivative melting at 165—166°; *piperonylidene-menthone* has not been isolated, but the *hydroxylamine* derivative forms colourless needles melting at 173—174°. M. A. W.

Action of Salicylic Acid on Terebenthene. E. TARDY (*J. Pharm. Chim.*, 1904, 20, [vi], 57—58).—When salicylic acid is boiled with terebenthene, a bornyl salicylate is formed, which melts at 44—45° and has $[\alpha]_D - 34^\circ 20'$. The compound displays triboluminescence, and is soluble in alcohol and ether, but insoluble in water.

G. D. L.

Preparation of Solid Camphene. CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING (D.R.P. 153924. Compare this vol., i, 680).—Solid camphene, free from chlorine, is readily obtained by the action of alkali hydroxides or ammonia on pinene hydrochloride dissolved in solutions of alkali soaps. When pinene hydrochloride is heated with dry powdered soap, the product is also free from chlorine, but a large excess of alkali soap is required. In solution, only $\frac{1}{2}$ mol. of soap is necessary. C. H. D.

Constituents of the Ethereal Oil of "Amorpha Fruticosa." VITTORIO PAVESI (*Chem. Centr.*, 1904, ii, 224; from *Rend. R. Ist. Lomb. sci. lett.*, [ii], 37, 487—494).—The portion of the oil boiling below 250° contains a terpene boiling between 150° and 220°, having $n_D 1.4811$ at 15.5° and a sp. gr. 0.8717 at 15°. The portion boiling at 250—270° contains cadinene and another sesquiterpene which has $n_D 1.50652$ at 15° and a sp. gr. 0.916 at 15°; it forms a liquid hydrochloride and resembles clovene. It is possibly a new sesquiterpene, $C_{15}H_{24}$ for which the name *amorphene* is suggested. N. H. J. M.

Composition of Patchouli Oil. HUGO VON SODEN and WILHELM ROJAHN (*Ber.*, 1904, 37, 3353—3355. Compare this vol., i, 604).—Patchouli oil was fractionated: two fractions of sp. gr. 0.984 and 1.002 at 15° respectively, consisting mainly of patchouli alcohol, whilst other two fractions of sp. gr. 0.946 and 0.964 respectively at 15° were submitted to further fractionation and yielded a fraction A with the sp. gr. 0.930—0.940 at 15° and α_D about -50° , and a fraction B with the sp. gr. 0.930—0.940°. After fraction A had been hydrolysed, it yielded a

sesquiterpene, $C_{15}H_{24}$, boiling at $264-265^\circ$ under 750 mm. pressure and having the sp. gr. 0.9335 at 15° and $d_D -58.45'$ at 20° . After fraction B had been hydrolysed, it yielded a sesquiterpene, with the sp. gr. 0.930 at 15° and $d_D 0.45'$ and boiling at $273-274^\circ$ under the ordinary pressure.
A. McK.

Caoutchouc Substances containing Oxygen. PAUL ALEXANDER (*Chem. Centr.*, 1904, ii, 705—706; from *Dresd. Gummi-Zeit.*, 18, 867—869. Compare Weber, this vol., i, 331).—Dry pontianac (Dead Borneo, Beck) contains 80 per cent. of substances soluble in acetone, of which the main component is a compound $C_{25}H_{40}O$, or more probably $C_{50}H_{80}O_2$. This substance melts at 161° and is the least soluble in acetone. The quantity of material insoluble in acetone never amounts to more than 15 per cent. of the dry pontianac. Analysis of the substance obtained after purifying a sample, which was more than 3 years old, by dissolving in chloroform and precipitating with ether, indicated the composition $C_{10}H_{16}$, and Weber's nitrogen dioxide additive product (*loc. cit.*) had the composition $C_{10}H_{16}O_4N_2$.

Guayrule caoutchouc, obtained from one of the Mexican *Compositæ*, was found to contain 60.3 per cent. of pure caoutchouc when tested by Weber's nitrogen dioxide method. The portion insoluble in acetone had the composition $C_{10}H_{16}$, but the nitrogen dioxide compound appeared to contain less carbon and hydrogen and more nitrogen than the normal additive product. The presence of caoutchouc substances rich in oxygen could not be detected.
E. W. W.

Presence of Esters of Cinnamic Acid in Specimens of Gutta-percha. PIETER VAN ROMBURGH (*Ber.*, 1904, 37, 3440—3443).—Two esters of cinnamic acid have been isolated from the resin of crude gutta-percha obtained from *Palaquium calophyllum* from Java. The one ester melts at $145-149^\circ$, and the other, which is identical with Tschirch's crystalalban (this vol., i, 76), melts at 242° (corr.), and on hydrolysis yields cinnamic acid and an alcohol melting at 210° . The alcohol somewhat resembles cholesterol. Its acetate melts at 212° and its benzoate at 262° .

Other specimens of gutta-percha yield the same products, but that from *Payena Leerii* appears not to contain esters of cinnamic acid.

J. J. S.

Simple Mode of Preparing Synthetic Populin. LEONARD DOBBIN and ALEX. D. WHITE (*Pharm. J.*, 1904, [iv], 19, 233—234).—Populin (benzoylsalicin) can be readily synthesised by the action of benzoyl chloride on salicin in presence of aqueous potassium hydroxide according to the Schotten-Baumann method.
E. G.

Saponin Substances. RUDOLF KOBERT (*Chem. Centr.*, 1904, ii, 450—451; from *Stuttgart. Verlag von Ferdinand Enke*, 1904. Compare Atstr., 1893, i, 424).—Saponin substances are more or less completely salted out by means of ammonium sulphate, the precipitation taking place more readily from warm solutions; quillajic acid and quillaja-

sapotoxin may be separated in this way, the former being completely precipitated, but not the latter. The Levantine sapotoxin is not identical with that of quillaja bark, since it is only partially precipitated by ammonium sulphate. Cyclamin from sow-bread, melanthin of *Nigella sativa*, chamælinin, sarsaponin, the neutral and acid saponins of guaiacum bark and leaves, polygalic acid of Senega root, and cereic acid are also precipitated by the sulphate.

Radix saponariæ rubræ contains two saponins, saporubric acid and saporubrin; the former is precipitated by ammonium sulphate, but not the latter. Other glucoside-substances, such as solanin, solanein, helleborein, ipecacuanhic acid, and condurangin are also precipitated by ammonium sulphate. When the saponins or sapogenins are salted out of solutions containing natural or artificial colouring matters, such as the dye contained in *Aplysia*, methylene-blue, neutral-red, methyl-violet, cyanin, &c., the dye is partly carried down by the precipitate; the colouring matter of blood is not, however, affected. Dyes are also extracted by aqueous solutions of the saponins and of condurangin through permeable membranes. The saponins resist the action of most animal enzymes, but are attacked by extracts of spiders, Russian tarantula, and dried ant pupæ with formation of a small quantity of sugar. When introduced into the blood in doses which are not fatal, the saponins do not, as a rule, cause hæmoglobinuria; cyclamin, parillin, sarsaponin, smilasaponin, monesin, and sapotin are exceptions, however, in this respect. Cyclamin also causes local coagulation of fibrin and thrombosis. The saponins which show the strongest hæmolytic action, when tested in glass vessels, also induce hæmoglobinuria most rapidly, but in the latter case the antitoxins of the serum play an important part. The hæmolytic action of each saponin on blood which has been diluted to 100 times its volume with sodium chloride solution has a certain value which is independent of the nature of the blood; guinea-pig blood is, however, especially sensitive.

The extraction of quillajic acid, polygalic acid, and the saponin acids of guaiacum from aqueous solutions by means of amyl or isobutyl alcohol is greatly facilitated by heating or by adding ammonium sulphate, but the extraction of sapotoxin is not affected. The saponin substances give the same reaction with ferric chloride and potassium ferricyanide as the corpse alkaloids, but in some cases only after warming. Quillajic acid and sapotoxin reduce warm ammoniacal solutions of silver or of gold chloride. The hæmolytic action of sapotoxin is due to its combination with the lecithin or cholesterol of the red corpuscles, and by this means causes the solution of the cells. These compounds may be prepared by heating the components in presence of water; the lecithin sapotoxin destroys the vitality of protoplasm and has a hæmolytic action, whilst the cholesterol compound is not poisonous.

When quillajic acid and sapotoxin are injected into the blood of rabbits in gradually increasing doses, the organism becomes immune to a certain limit. The saponin substances of quillaja bark have an effect on the muscular, but not on the nervous, system of the heart; living hearts of frogs, *Torpedo ocellata* and *Aplysia limacina* are quickly

killed. One part of quillajic acid or sapotoxin in 300,000 of sea water is sufficient to cause the death of fish; other animals are less affected, and crabs scarcely at all, the chitin membrane of the gills preventing the access of these compounds. Cholesterol sapotoxin is not poisonous even to fish. The acid is the only component of quillaja bark which has the same physiological action as the bark itself. Ten times the quantity of quillajic acid is required to cause death by subcutaneous injection in the case of frogs and other invertebrata as in the case of warm-blooded animals. Cephalopods are more affected by intravenous than by subcutaneous injection. Quillajic acid and sapotoxin act on the red corpuscles of the blood of bony and cartilaginous fish about as strongly as on those of ox-blood. For hæmolytic experiments, the blood may be diluted with a 3·5 per cent. solution of sodium chloride instead of with physiological sodium chloride solution. The white corpuscles of cephalopods, snails, crabs, and *Gephyreæ* are dissolved by saponin substances if the concentration of the latter is sufficiently great, solution being caused by the formation of lecithin and cholesterol compounds. The use of the poisonous saponin substances of quillaja bark and red soap-wort in the manufacture of aerated lemonade and in the preparation of cod-liver and castor-oil emulsions should be legally prevented; the harmless neutral saponins of guaiacum bark might be used as substitutes.

E. W. W.

The Sugar of the Aloins. EUGÈNE LÉGER (*J. Pharm. Chim.*, 1904, [vi], 20, 145—148. Compare Abstr., 1903, i, 356).—The aloins cannot be hydrolysed by means of dilute acids and soluble ferments, but when left in contact during prolonged periods with alcohol, resolution occurs with formation of a sugar. This compound, which has the properties of a pentose, is formed both by barbaloin and *iso*-barbaloin, and is named by the author *aloinose*. This result confirms the view that the aloins are glucosides, as previously suggested by the author.

G. D. L.

Decomposition Products of Aloin. OTTO A. OESTERLE and ALEXIS BABEL (*Chem. Centr.*, 1904, ii, 340; from *Schweiz. Woch. Pharm.*, 42, 329—332).—Tilden's aloexanthin (this Journal, 1877, ii, 267) is shown to be impure rhein, which according to Hesse is tetrahydroxymethylanthraquinone. It is totally different in its behaviour from Seel's tetrahydroxymethylanthraquinone (Abstr., 1901, i, 92). It is uncertain whether the aloechrysin (obtained from the impure rhein) stands in the same relation to rhein as Seel's hydrated methyltrihydroxyanthraquinone oxide to his tetrahydroxymethylanthraquinone.

N. H. J. M.

Lactucon [Lactucerin]. CÆSAR POMERANZ and F. SPERLING (*Monatsh.*, 1904, 25, 785—792. Compare Kassner, Abstr., 1887, 605; Hesse, Abstr., 1888, 722).—Lactucerin, obtained from *Lactucarium Germanicum* by extraction with light petroleum and purified by treatment with ether and animal charcoal and by repeated recrystallisation from alcohol, has the molecular composition $C_{28}H_{36}O_2$, crystallises in

small needles, melts at 184° , has neither odour nor taste, has $[\alpha]_D + 50^{\circ}$ at 18° , and is easily soluble in ether, benzene, chloroform, light petroleum, carbon disulphide, or hot alcohol, but is insoluble in water. When boiled with alcoholic potassium hydroxide, it is hydrolysed to acetic acid and *lactucol*, $C_{21}H_{34}O$, which crystallises in small, white needles, melts at 154.5° , and yields lactucerin when boiled with sodium acetate and acetic anhydride. The action of bromine on lactucerin in carbon disulphide solution leads to the formation of an *additive* product, $C_{23}H_{36}O_2Br_2$, which crystallises in small, yellow needles and decomposes when heated. G. Y.

Researches on Scammonin. PAUL REQUIER (*J. Pharm. Chim.*, 1904, [vi], 20, 148—151).—On lixiviation of scammony root with alcohol, it yields 7.2 per cent. of purified scammonin. The water used in washing the crude compound contains a levorotatory tannin, giving an intense green coloration with ferric salts. The aqueous liquids also contain a dextrorotatory sugar, probably a pentose, and a nitrogen compound giving ammonia with potash and nitrogen with hypobromite. G. D. L.

Brazilin and Hæmatoxylin. VIII. JOSEF HERZIG and JACQUES POLLAK (*Monatsh.*, 1904, 25, 871—893. Compare Abstr., 1894, i, 341; 1896, i, 379; 1899, i, 381, 821; 1901, i, 478; 1902, i, 482; 1903, i, 270, 713; this vol., i, 333).—[With EUGEN G. GALITZENSTEIN.]—The isomeride of trimethylbrazilone can be titrated with a normal alkali with phenolphthalein as indicator; it is only partially precipitated, from its solution in an aqueous alkali hydroxide, on saturation with carbon dioxide, the remainder being precipitated unchanged on addition of a mineral acid. When warmed with potassium hydroxide and methyl iodide in alcoholic solution, or when treated with diazomethane, it forms the *methyl ether*, $C_{16}H_8O_2(OMe)_4$, which crystallises from alcohol, melts at $82-83^{\circ}$, remains unchanged when boiled with sodium acetate and acetic anhydride, but is hydrolysed to its parent substance, $C_{16}H_8O_2(OMe)_3 \cdot OH$, when treated with alcoholic or aqueous potassium hydroxide. No oxime could be obtained from the isomeride of trimethylbrazilone or from α -trimethyldehydrobrazilin.

The sulphate obtained by the action of sulphuric acid on triacetyl-brazilin in glacial acetic acid solution is acetylated, with or without the presence of zinc dust, to triacetyl-brazilin; when treated with water or sodium acetate solution, it is decomposed yielding an amorphous substance. When boiled with sodium acetate, zinc dust and glacial acetic acid for about half-an-hour, and again after addition of acetic anhydride, the sulphate yields tetra-acetyl-brazilin. On hydrolysis with hydrogen chloride in alcoholic solution, tetra-acetyl-brazilin yields a yellow, amorphous *substance*, which dissolves in aqueous alkalis to a colourless solution, which becomes red on boiling; on acetylation, without zinc dust, it forms tetra-acetyl-brazilin.

[With BR. VOUG.]—Dinitrotetramethylhæmatoxyline does not form an acetyl derivative when boiled with sodium acetate and acetic anhydride (compare Gilbody and Perkin, *Proc.*, 1899, 15, 27). When treated with potassium hydroxide in aqueous solution, it yields

6-nitrohomoveratrole, tetramethoxydinitrodibenzyl (Gilbody and Perkin, *Trans.*, 1902, 81, 1049), and 2-carboxy-5:6-dimethoxyphenoxyacetic acid (Perkin and Yates, *Trans.*, 1902, 81, 241). The *methyl* ester, $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_2\text{O}(\text{OMe})_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$, of the latter forms white crystals and melts at $84-87^\circ$. G. Y.

Hæmatein and Hæmalum. PAUL MAYER (*Chem. Centr.*, 1904, ii, 228; from *Zeit. wiss. Mikros.*, 20, 409—411).—Hæmatein is readily obtained by dissolving 1 gram of hæmatoxylin in 10 c.c. of boiling water, adding 0.2 gram of sodium iodate dissolved in 2 c.c. of water. The hæmatein is separated by filtration after 1 or 2 hours, washed with cold water, and dried at the ordinary temperature or with moderate heat. Brazilein is prepared in a similar manner. When alum (50 grams) is added to hæmatoxylin (1 gram) and sodium iodate (0.2 gram), hæmalum is obtained. Chloral hydrate and citric acid are added to enable it to be kept. N. H. J. M.

Probable Identity of Phylloerythrin and Cholehæmatin. LEON MARCHLEWSKI (*Bull. Acad. Sci. Cracow*, 1904, 6, 276—280).—The spectroscopic examination of chloroform solutions of phylloerythrin and cholehæmatin reveals four absorption bands in the visible part of the spectrum, which, in regard to position and relative intensity, appear to be identical. The two bands in the ultra-violet differ somewhat, but this is probably due to impurities in the cholehæmatin solution employed, and the identity of the two substances seems very probable. H. M. D.

Colouring Matters of Rosa Gallica. WILLIAM A. H. NAYLOR and E. J. CHAPPEL (*Pharm. J.*, 1904, [iv], 19, 231—233).—The petals of *Rosa gallica* contain two colouring matters, one yellow, the other red. The yellow colouring matter, $\text{C}_{15}\text{H}_{12}\text{O}_6$, crystallises from dilute alcohol in minute needles, does not melt when heated to 220° , gives a brownish-black coloration with ferric chloride, and an orange-red precipitate with lead acetate; it slowly reduces boiling Fehling's solution, and imparts an orange-yellow coloration with a green fluorescence to warm sulphuric acid. This substance is not identical with quercitrin, as was supposed by Filhol (*Rep. Pharm.*, 1863). When heated with potassium hydroxide at $210-230^\circ$, it yields phloroglucinol and another substance which is probably protocatechuic acid. The yellow colouring matter is hydrolysed with difficulty by sulphuric or hydrochloric acid, red amorphous products being formed.

The red colouring matter was obtained as a deep red, amorphous powder, soluble in water or alcohol. The crystalline alkali salts of this substance described by Senier (*Abstr.*, 1877, ii, 502) could not be obtained. E. G.

Behaviour of Wool Fibre to Certain Acid Dyes. Contribution to the Theory of Dyeing. EDMUND KNECHT (*Ber.*, 1904, 37, 3479—3484. Compare *Abstr.*, 1889, 49, 869).—Experiments made with orange G and crystal-ponceau, ponceau 2G and xylidine-

ponceau, orange II and "Echt" red A, "Echt" acid fuchsin B, the corresponding naphthylamine dye, picric acid, *s*-trinitroresol, and *s*-trinitroxylenol indicate that the amounts of dye taken up by the wool fibre are in the ratios of the molecular weights of the dyes.

The amount of dye taken up does not vary much with the amount of water present. The actual amount taken up was determined by estimating the amount originally present in solution and then the amount left after dyeing. All estimations were made by aid of titanium trichloride. This method, however, did not yield good results with trinitroresol and trinitroxylenol.

In the case of crystal-ponceau, the curve representing the relationship between amount of dye (in per cent.) present and amount taken up by the fibre is represented by a straight line until 17 per cent. has been taken up, and then rises rapidly and runs nearly parallel with the vertical ordinate.

J. J. S.

Formation of Furoyl Derivatives by means of Pyromucic Chloride. Synthesis of Pyromykuric Acid. ERICH BAUM (*Ber.*, 1904, 37, 2949—2961).—A number of furoyl compounds have been prepared by the action of pyromucic chloride on phenols, amines, and amino-acids in aqueous alkali hydroxide or carbonate, or in pyridine solution. The reaction does not take place with methylamine. The resulting products resemble the corresponding benzoyl compounds, than which they are usually more soluble. The furoyl compounds are easily hydrolysed by boiling with barium hydroxide in aqueous solution; hydrolysis, by means of boiling hydrochloric acid, is usually accompanied by further decomposition.

Pyromykuric acid (Jaffé and Cohn, *Abstr.*, 1887, 1032) is formed by the action of pyromucic chloride on glycine in slightly alkaline solution. The *ethyl* ester crystallises in long, white, silky needles and melts at 77°.

The following new compounds are described; the temperatures given are melting points:—

Phenyl pyromucate, $C_4OH_3 \cdot CO_2Ph$, crystallises in prisms, 41.5°; *m*-phenylene dipyromucate, $C_6H_4(C_5H_3O_3)_2$, crystallises in nacreous plates, 128—129°. *Difuroylhydroxamic acid*, $(C_4OH_3 \cdot CO)_2N \cdot OH$, crystallises in prisms, 180°; when heated with an alkali hydroxide and neutralised, it gives a dark violet coloration with ferric chloride. *Furoylpiperidide*, $C_5H_3O_2 \cdot C_5H_{10}N$, crystallises in glistening, brittle rhombohedra, 58°; *ethylenedifuramide* crystallises in white prisms, 200°; *furoyl-p-toluidide* forms glistening prisms, 107.5°; *furoyl-m-toluidide* crystallises in glistening prisms, 87°; *furoyl-o-toluidide* separates from petroleum in long, glistening needles, 62°. *Furoylalanine*, $C_5H_3O_2 \cdot C_3H_6O_2N$, forms glistening, hexagonal plates, 169°; the barium, $(C_8H_8O_4N)_2Ba$, and the silver, $C_8H_8O_4NAg$, salts are described; the *ethyl* ester, $C_8H_8O_4NEt$, crystallises in small, hexagonal plates, 71—72°. *Furoyl-l-aspartic acid*, $C_5H_3O_2 \cdot C_4H_6O_4N$, forms four-sided prisms, 162—163°, $[\alpha]_D + 43.17^\circ$ at 20°. *Furoyl-l-asparagine* crystallises in colourless prisms, 172—173°, $[\alpha]_D + 19.75^\circ$ at 20°; the barium, $(C_9H_9O_5N_2)_2Ba \cdot 2H_2O$, the copper, $(C_9H_9O_5N_2)_2Cu \cdot H_2O$, and the silver, $C_9H_9O_5N_2Ag$, salts are described. *Phenylpyromykuric acid*, $C_{13}H_{11}O_4N$,

formed from α -phenylaminoacetic acid, crystallises in clusters of slender, white needles, 178—179°; the *barium* salt, $(C_{13}H_{10}O_4N_2)_2Ba$, crystallises in prisms. G. Y.

A Second Synthesis of Chrysin. STANISLAUS VON KOSTANECKI and VICTOR LAMPE (*Ber.*, 1904, 37, 3167—3168. Compare Fainberg and Kostanecki, this vol., i, 682; Kostanecki and Tambor, this vol., i, 426; Kostanecki, Lampe, and Tambor, this vol., i, 763).—3:6:8-

Tribromo-5:7-dimethoxyflavanone,
$$\begin{array}{c} C(OMe):CBr \cdot C-O-CHPh \\ | \\ CBr:C(OMe) \cdot C \cdot CO \cdot CHBr \end{array}$$
 prepared by brominating 5:7-dimethoxyflavanone, crystallises from benzene in prisms and melts and decomposes at 174—175°. When boiled with alcoholic potassium hydroxide, it yields 6:8-dibromo-5:7-dimethoxyflavone,
$$\begin{array}{c} C(OMe):CBr \cdot C-O-CHPh \\ | \\ CBr:C(OMe) \cdot C \cdot CO \cdot CH \end{array}$$
 which separates from a mixture of

glacial acetic acid and ethyl alcohol in needles and melts at 253°. When the latter compound is boiled with hydriodic acid, it forms 5:7-dihydroxyflavone (chrysin),
$$\begin{array}{c} C(OH):CH \cdot C-O-CHPh \\ | \\ CH:C(OH) \cdot C \cdot CO \cdot CH \end{array}$$
 A. McK.

Flavindogenides. A. KATSCHALOWSKY and STANISLAUS VON KOSTANECKI (*Ber.*, 1904, 37, 3169—3172).—The methylene group in

flavanone, $C_6H_4 \begin{array}{l} \diagup O-CHPh \\ \diagdown CO \cdot CH_2 \end{array}$, is very reactive on account of its proximity to the carbonyl group, and reacts readily with bromine and with nitrous acid to form 3-bromoflavanone and *is*onitrosoflavanone respectively. It is now shown that the hydrogen atoms of this methylene group may be replaced by aldehyde groups to form compounds analogous to indogenides, oxindogenides, deoxycarbindogenides, and carb-

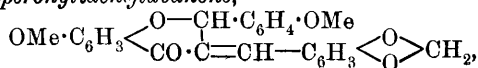
indogenides, and which are termed flavindogenides. They are prepared by saturating a hot alcoholic solution of a mixture of flavanone and aldehyde with hydrogen chloride and then adding water, when the dye separates and may be crystallised from alcohol.

From 6-ethoxyflavanone,
$$\begin{array}{c} CH:CH \cdot C-O-CHPh \\ | \\ OEt \cdot C=CH \cdot C \cdot CO \cdot CH_2 \end{array}$$
, the following compounds were prepared:

6-Ethoxy-3-benzylideneflavanone, $OEt \cdot C_6H_5 \begin{array}{l} \diagup O-CHPh \\ \diagdown CO \cdot C:CHPh \end{array}$, which separates from alcohol in leaflets and melts at 106°.

6-Ethoxy-3-anisylideneflavanone separates in spear-shaped crystals and forms a magenta solution with concentrated sulphuric acid. 6-Ethoxy-3-veratrylideneflavanone crystallises in pyramids, melts at 145—146°, and forms a violet solution with concentrated sulphuric acid.

By the action of piperonal on 6:2'-dimethoxyflavanone, 6:2'-dimethoxy-3-piperonylideneflavanone,



is formed; this separates in yellow prisms, melts at 207—209°, and yields a violet-red coloration with concentrated sulphuric acid.

7:8-Dimethoxy-3-anisylideneflavanone forms tiny plates, melts at 186°, and gives an orange coloration with concentrated sulphuric acid. 7:8-Dimethoxy-3-veratrylideneflavanone forms tiny plates, melts at 196°, and gives a red coloration with concentrated sulphuric acid.

7:8-Dimethoxy-3-piperonylideneflavanone separates from alcohol in pyramids, melts at 185°, and gives a magenta coloration with concentrated sulphuric acid.

A. MCK.

Xanthonium and Thioxanthonium Compounds. HANS BÜNZLY and HERMAN DECKER (*Ber.*, 1904, 37, 2931—2938. Compare *Abstr.*, 1900, ii, 518; 1902, i, 50; this vol., i, 344).—Xanthonium and thioxanthonium compounds may be prepared by Grignard's reaction, and show a complete parallelism in properties and chemical behaviour with acridinium compounds. They are of interest as containing quadrivalent oxygen or sulphur, combined with three carbon-valencies.

Phenylxanthenol (carbinol form of *phenylxanthonium hydroxide*), $C_6H_4 \begin{array}{c} \text{CPh(OH)} \\ \diagup \quad \diagdown \\ \text{O} \end{array} C_6H_4$, prepared by heating xanthone in benzene solution with magnesium phenyl bromide, forms colourless prisms and melts at 158.5—159°. It sublimes without decomposition and dissolves readily in chloroform or benzene, sparingly in light petroleum. The *ethyl ether* forms terrace-like crystals and melts at 102—103°; the *methyl ether* forms colourless needles and melts at 96—97°.

The carbinol dissolves in mineral acids to orange-red solutions, becoming slowly paler on dilution with water, the carbinol being precipitated. Heating favours the formation of the oxonium modifications.

Phenylxanthonium ferrichloride, $C_{19}H_{13}OCl_2FeCl_3$, forms glistening, reddish-brown scales and melts at about 174°. The *mercurichloride* forms large, red prisms and begins to melt at about 230°, decomposing at 235°. The *cadmiobromide* forms purple plates; the *aurichloride* forms golden needles. These salts are stable in air and are hydrolysed by warm water. Bromine water precipitates *phenylxanthonium tribromide* from solutions of xanthonium salts, forming red scales, melting and decomposing at 168—170°. The *tri-iodide* forms glistening, black needles and dissolves in chloroform or glacial acetic acid to dark violet solutions.

[With C. WITTMANN].—*Phenylthioxanthenol* (carbinol form of *phenylthioxanthonium hydroxide*), $C_6H_4 \begin{array}{c} \text{CPh(OH)} \\ \diagup \quad \diagdown \\ \text{S} \end{array} C_6H_4$, from thioxanthone and magnesium phenyl bromide, separates from benzene and light petroleum in compact, drusy masses and melts at 105—106°. The *ethyl ether* forms thick crystals and melts at 76—77°.

Phenylthioxanthonium salts form intensely red solutions and are more stable than the corresponding oxonium salts. The *ferrichloride* forms dark red needles and melts at 169°; the *cadmiobromide* forms

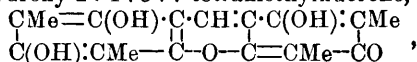
broad, dark red needles, and the *mercurichloride* dark red prisms. The *tribromide* forms dark red needles and melts at about 180° .

C. H. D.

Constitution of Trihydroxytetramethylfluorone. FRANZ WENZEL and A. SCHREIER (*Monatsh.*, 1904, 25, 657—681. Compare Abstr., 1900, i, 308; this vol., i, 518).—When heated together at 140 — 150° in glacial acetic acid solution, in presence of concentrated sulphuric acid, dimethylphloroglucinol and 2:4:6-trihydroxy-3:5-dimethylbenzaldehyde form a dark red solution, which gradually deposits an additive compound of 1:3:8-trihydroxy-2:4:5:7-tetramethylfluorone and sulphuric acid, $C_{17}H_{16}O_5, H_2SO_4$. This crystallises in delicate, glistening, matted, red needles, decomposes when heated, is stable towards alcohol, but loses sulphuric acid when treated with water. If the condensation takes place in presence of hydrochloric acid, the additive compound with hydrochloric acid is obtained. This is also formed as a by-product in the formation of trihydroxydimethylbenzaldehyde by the action of hydrogen chloride on dimethylphloroglucinol and hydrocyanic acid. It crystallises in slender, glistening, red needles and yields trihydroxytetramethylfluorone on prolonged boiling with alcohol.

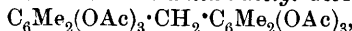
The compound $C_{17}H_{16}O_5, H_2SO_4$ is also formed when methylenebisdimethylphloroglucinol (Böhm, Abstr., 1902, i, 39) is warmed with concentrated sulphuric acid.

1:3:8-Trihydroxy-2:4:5:7-tetramethylfluorone,



crystallises from resorcinol in long, blood-red needles, from acetic acid in dark red plates; like its acid additive compounds, when heated, it decomposes without melting; it is only very slightly soluble in alcohol or glacial acetic acid.

The action of acetic anhydride on methylenebisdimethylphloroglucinol leads to the formation of a *hexa-acetyl* derivative,



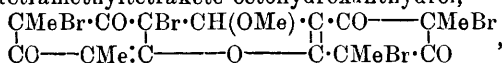
which crystallises in white leaflets, melts at 232 — 233° , and, on hydrolysis with concentrated sulphuric acid, yields trihydroxytetramethylfluorone.

Reduction of trihydroxytetramethylfluorone with sodium amalgam and water leads to the formation of tetrahydroxytetramethylxanthen, $CMe\cdot C(\text{OH})\cdot C\cdot CH_2\cdot C\cdot C(\text{OH})\cdot CMe$
 $C(\text{OH})\cdot CMe-\text{C}-O-\text{C}-CMe\cdot C\cdot OH$, which crystallises in clusters of white needles, melts at 320 — 324° , and is soluble in alcohol, acetone, or ether. When dry, it is comparatively stable, but when moist it is rapidly oxidised; with ferric chloride, it gives a dark red coloration, and when warmed with sulphuric acid it is converted, but less easily than methylenebisdimethylphloroglucinol, into the sulphuric acid compound of trihydroxytetramethylfluorone. The *tetra-acetyl* derivative of tetrahydroxytetramethylxanthen crystallises in white needles, melts at 268 — 270° , and forms a fluorescent solution in concentrated

sulphuric acid. This acetyl compound is oxidised by chromic acid in glacial acetic acid solution to the *tetra-acetyl* derivative of tetrahydroxy-tetramethylxanthidol, $C_6Me_2(OAc)_2 \langle \text{CH}(\text{OH}) \rangle C_6Me_2(OAc)_2$, which is also formed by the action of acetic anhydride and sodium acetate on 1:3:8-trihydroxy-2:4:5:7-tetramethylfluorone. It melts at $256-259^\circ$, and is reduced by zinc dust in glacial acetic acid solution to tetra-acetoxytetramethylxanthin.

The action of bromine on trihydroxytetramethylfluorone in methyl-alcoholic solution leads to the formation of a *bromo-derivative*,

$C_{17}H_{15}O_5Br$,
which crystallises in dark red needles, and of the *methyl ether* of tetrabromotetramethyltetrahydroxy-octahydroxanthidol,



which forms large, almost white crystals, which become yellow on exposure to air, red on exposure to light. It melts and decomposes at $155-160^\circ$ and is only slightly soluble in methyl or ethyl alcohols, but easily so in benzene or glacial acetic acid.

As the condensation of dimethylphloroglucinol and 2:4:6-trihydroxy-3:5-dimethylbenzaldehyde can take place only in one way, the experimental details now published confirm the fluorone constitution ascribed to the condensation products of salicylaldehyde and the homologues of phloroglucinol. G. Y.

The Indophenine Reaction. FRANZ W. BAUER (*Ber.*, 1904, 37, 3128—3130. Compare Bauer, this vol., i, 519).—A reply to Storch (this vol., i, 610) and to Liebermann and Pleus (this vol., i, 684).

A. McK.

Indophenines. HEINRICH OSTER (*Ber.*, 1904, 37, 3348—3352).—With ordinary substituted indophenines, as also with the analogous compounds which are formed from phthaloneimide and thiophen or from thiophthen and isatin, the mechanism of formation is identical, water being eliminated in every case (compare Bauer, this vol., i, 519; Liebermann and Pleus, this vol., i, 684). Thiophthen forms two distinct indophthenines according as it is combined with 1 or with 2 molecules of isatin. All indophenines form blue solutions with concentrated sulphuric acid.

Nitroindophenine, $NO_2 \cdot C_8H_3ON \cdot C_4SH_3$, prepared from nitroisatin and thiophen, is a dark blue powder, which forms a bright blue solution with concentrated sulphuric acid.

Carbindophenine, $C_9H_4O_2N \cdot C_4SH_3$, prepared from phthaloneimide and thiophen, is dark blue and forms a blue solution with concentrated sulphuric acid.

Monoisatinindophthenine, $C_8H_4ON \cdot C_6S_2H_3$, prepared by adding concentrated sulphuric acid to a solution of equal weights of isatin and thiophthen in glacial acetic acid, is a grey powder, which forms a reddish-blue solution with concentrated sulphuric acid; on exposure to light, it gradually becomes brown.

Di-isatinindophthenine, $C_6S_2H_2(C_8H_4ON)_2$, prepared by the action of

concentrated sulphuric acid on a solution of thiophthen (1 part) and isatin (3 parts) in glacial acetic acid, is a blue powder.

Bromoindophthennine, $C_8H_5ONBr \cdot C_6H_5S_2$, is a grey powder. *Carb-indophthennin*, $C_9H_4O_2N \cdot C_6H_5S_2$, prepared from phthaloneimide and thiophthen, is a bright green powder. Phenanthraquinone and thiophthen form a *compound*, $C_{18}H_{10}OS$, which separates in deep green flakes; the corresponding *compound*, $C_{20}H_{10}OS_2$, with thiophthen is a bright green powder. A. McK.

Caffearine, an Alkaloid from Coffee. L. GRAF (*Zeit. öffentl. Chem.*, 1904, 15, 279—281).—The existence of this alkaloid, which was isolated from coffee by Palladino (Abstr., 1894, i, 214; 1895, i, 629), having been doubted recently, the author states that having repeated Palladino's experiments he has succeeded in obtaining the alkaloid in a pure state. It may also be obtained in small quantities from aqueous infusions of raw coffee beans without using calcium hydroxide. Caffeine and proteids, when treated with the latter substance, do not yield caffearine. L. DE K.

isoCinchonine Bases. ZDENKO H. SKRAUP and RUDOLF ZWERGER (*Monatsh.*, 1904, 25, 894—906. Compare Abstr., 1903, i, 715).—When warmed on the water-bath with concentrated hydrochloric acid, *α-isocinchonine* yields a small amount of the sparingly soluble hydrochloride of hydrochlorocinchonine. The action of a saturated aqueous solution of hydrogen chloride on *α-isocinchonine* in a sealed tube at 100° leads to the formation of trihydrochlorocinchonine, the sparingly soluble hydrochloride of hydrochlorocinchonine, and a *hydrochloride* which is easily soluble in water, and, with ammonia, yields hydrochloro-*α-isocinchonine*, $C_{19}H_{23}ON_2Cl$, which crystallises in microscopic prisms and melts at 185—186°; the *sulphate*,

$(C_{19}H_{23}ON_2Cl)_2 \cdot H_2SO_4 \cdot 4H_2O$, crystallises in microscopic prisms, loses $4H_2O$ at 105°, and is sparingly soluble in water (Hesse, Abstr., 1893, i, 677). Hydrochloro-*α-isocinchonine* is also formed, along with hydrochlorocinchonine, by the action of concentrated hydrochloric acid on trichlorocinchonine at 100° under pressure. When the sparingly soluble sulphate is heated with alcoholic potassium hydroxide, it yields a base which melts at 247—248° and may be cinchonine.

The action of hydrochloric acid on *β-isocinchonine* and on *allocinchonine* leads to the formation of traces of hydrochlorocinchonine only. When warmed with saturated hydrobromic acid, *α-isocinchonine* yields the hydrobromide of hydrobromocinchonine.

α- and β-isocinchonines do not enter into reaction with chlorine in hydrochloric acid solution. Cinchonine forms an additive compound with chlorine, $C_{19}H_{22}ON_2Cl_2$, which melts at 217—218° (Koenigs, Abstr., 1892, 1011). A base of the same composition, which melts at 205—206° and is possibly identical with cinchonine dichloride, is formed by the action of chlorine on *allocinchonine*. G. Y.

Attempts to prepare Alkaloids of the isoQuinoline Series. MARTIN FREUND (*Ber.*, 1904, 37, 3334—3337. Compare Liebermann and Glawe, this vol., i, 765).—*α*-Substituted derivatives of hydrocotar-

nine may be prepared by the application of Grignard's reaction to cotarnine or to its salts, such as the hydrochloride or cyanide. Dihydrocotarnine, melting at 163—164°, may be prepared by Grignard's reaction with cotarnine, using ethylene bromide, methylene chloride, benzylidene chloride, or acetylene tetrachloride respectively. Hydrastinine behaves like cotarnine in these reactions.

By the application of Grignard's reaction to berberinal, α -derivatives of a dihydroberberine are formed; *benzylidihydroberberine* forms yellow rhombohedra and melts at 161—162°.

Anhydrocotarnine benzyl cyanide melts at 134° to a red liquid; its *hydrochloride* melts at 154—155°.

Anhydrocotarnine benzyl cyanide-methine methiodide,

$\text{CH}_2\text{:O}_2\text{:C}_6\text{H(OMe)(CH:CPh-CN)\cdot CH}_2\text{\cdot CH}_2\text{\cdot NMe}_3\text{I}$, separates from alcohol in plates and melts at 225—227°; trimethylamine is formed by warming it with alkali. A. McK.

Morphine. V. New Basic Products from Methylmorphimethine: Tetramethylethylenediamine and Dimethylaminoethyl Ether. LUDWIG KNORR (*Ber.*, 1904, 37, 3494—3498. Compare Abstr., 1903, i, 849).—Hydrogen chloride reacts with methylmorphimethine, probably forming in the first place chloroethyl-dimethylamine (Abstr., 1894, i, 430; and this vol., i, 854). In place of this base, however, a mixture of ethanoldimethylamine and tetramethylethylenediamine is obtained. The *platinichloride* of the latter base crystallises in characteristic, glistening leaflets, and blackens and decomposes at 250°; the *aurichloride* forms small needles and melts and decomposes at 212°; the *picrate* crystallises in needles and melts at 197°.

Sodium ethoxide decomposes methylmorphimethine, forming methylmorphol and *dimethylaminoethyl ether*, $\text{NMe}_2\text{\cdot CH}_2\text{\cdot CH}_2\text{\cdot OEt}$. The *aurichloride* forms flat, glistening lozenges, melting at 85—90°, and dissolves in hot water; the *picrate* crystallises from hot water in leaflets and melts at 119—121°; the *methiodide* (choline hydriodide ethyl ether) forms short prisms and melts at 160—165°.

Codeine methiodide and sodium ethoxide yield the same products, together with dimethylamine. C. H. D.

Morphine. VI. Dimethylaminoethyl Ether as a Decomposition Product from Thebaine Methiodide and Codeinone Methiodide. LUDWIG KNORR (*Ber.*, 1904, 37, 3499—3504).—Thebaine methiodide reacts readily with sodium ethoxide on warming to form thebaol and tetramethylethylenediamine (compare Freund, Abstr., 1897, i, 495). Thebaine methiodide is also decomposed on heating with alcohol at 160—165°, forming thebaol and dimethylaminoethyl ether, together with a small quantity of dimethylamine.

Alcohol also decomposes codeinone methiodide at 150—160°, yielding dimethylaminoethyl ether and 4:6-dihydroxy-3-methoxyphenanthrene, the latter being isolated in the form of its acetyl derivative.

The primary product in these cases is probably dimethylvinylamine, which, however, has not yet been prepared. At the moment of

formation, it combines with alcohol, forming dimethylaminoethyl ether. In similar manner, in the decomposition by acetic anhydride (Abstr., 1903, i, 849), the hydramine acetate is formed from the vinyl base. The tetramethylethylenediamine obtained above results from the combination of the vinyl base with dimethylamine.

The author's former assumption, that morphine contains an oxazine ring, is probably incorrect, and morphine and thebaine must be regarded as containing an oxygen bridge, $C_6H_5 \begin{array}{c} \diagup O \diagdown \\ \diagdown CH:CH \diagup \end{array} C_6H_5$, such as has been found in morphenol derivatives by Vongerichten (Abstr., 1900, i, 248).
C. H. D.

Papaverine. MARTIN FREUND and HEINRICH BECK (*Ber.*, 1904, 37, 3321—3324).—When papaveraldine (Goldschmiedt, Abstr., 1886, 478) in the form of its sulphate is subjected to electrolytic reduction, using a leaden cathode, a secondary amine, $C_{20}H_{25}O_4N$, *isotetrahydro-papaverine*, is obtained. It is best isolated in the form of the *nitroso-amine*, which melts at 138° . The *hydriodide*, $C_{20}H_{25}O_4N, HI$, crystallises from alcohol in colourless prisms, which sinter at 245° and melt at 255° . The free base has only been obtained as a syrup. Its physiological properties have been examined.
J. J. S.

Constitution of Sparteine. RUDOLF WACKERNAGEL and RICHARD WOLFFENSTEIN (*Ber.*, 1904, 37, 3238—3244).—Sparteine, $C_{15}H_{26}N_2$, can under no conditions be reduced, and is not therefore an unsaturated base, as Ahrens (Abstr., 1897, i, 231) claimed. Hydrogen peroxide converts it into sparteine oxide, melting at 127 — 128° , in which the oxygen is doubly linked to nitrogen. Further, sparteine contains no methyl group attached to nitrogen, as supposed by Ahrens. The authors consider it to be a dicyclic saturated ring system, one nitrogen being in a pyridine and one in a pyrrolidine ring. It boils at 326° , forms a *picrate* melting at 199 — 200° , a *platinichloride* decomposing at 244 — 257° , an *aurichloride* decomposing at 175 — 184° , a *hydriodide* melting at 226 — 228° , a *dihydriodide* melting at 257 — 258° , an *oxalate* crystallising with a molecule of alcohol and melting at 138 — 140° , and a *methobromide* melting and decomposing at 219° .
E. F. A.

Synthesis of Polypeptides. V. Derivatives of Prolin (Pyrrolidine-2-carboxylic Acid). EMIL FISCHER and EMIL ABDERHALDEN (*Ber.*, 1904, 37, 3071—3075. Compare Abstr., 1903, i, 465, 799, 607, 800; this vol., i, 652).—The proline used was derived from gelatin and the method of isolation is described in detail. α -*Bromoisohexoyl-prolin* (inactive), $CHMe_2 \cdot CH_2 \cdot CHBr \cdot CO \cdot C_4NH_7 \cdot CO_2H$, prepared by condensing the constituents in presence of normal sodium hydroxide, crystallises from acetone in colourless needles melting at 163° (corr.). The active *bromoisohexoylproline* prepared from *l*-proline melts at 154 — 158° (corr.) and crystallises from acetone in microscopic prisms.

Leucylproline, $CHMe_2 \cdot CH_2 \cdot CH(NH_2) \cdot CO \cdot C_4NH_7 \cdot CO_2H$, formed by

the action of aqueous ammonia on the bromo-derivative, crystallises from ethyl acetate in aggregates of needles, melts between 116° and 119° (corr.), is easily soluble in water, and has a bitter taste. On heating at 145°, water is eliminated and *leucylprolinanhydride* is formed; this crystallises from water in minute needles melting between 117° and 121° (corr.).
E. F. A.

A New Method for breaking down Cyclic Amines. JULIUS VON BRAUN (*Ber.*, 1904, 37, 2915—2922).—The action of phosphorus pentachloride on aromatic acylamines (this vol., i, 731) may be employed to break down the ring, producing either chlorinated primary amines or dichlorinated hydrocarbons.

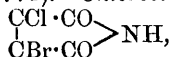
Benzoylpiperidine reacts with phosphorus pentachloride at 120°, forming the imide chloride, $\text{CClPh}\cdot\text{N}\cdot[\text{CH}_2]_5\cdot\text{Cl}$. On decomposing with water, distilling with steam, and then distilling the residue under reduced pressure, *benzoyl-ε-chloroamylamine*, $\text{COPh}\cdot\text{NH}\cdot[\text{CH}_2]_5\cdot\text{Cl}$, is obtained in white crystals melting at 66°. Hydrochloric acid hydrolyses it at 170—180° to ε-chloroamylamine (Gabriel, *Abstr.*, 1892, 717).

If the benzoylpiperidine and phosphorus pentachloride are heated until the reaction ceases and the phosphorus oxychloride is removed by distillation, the residue may be distilled under reduced pressure, and consists of benzonitrile and αε-dichloropentane. The former may be removed by hydrolysis with hydrochloric acid.

αε-Dichloropentane is a colourless liquid, boiling and slightly decomposing at 176—178° and boiling at 79—80° under 21 mm. pressure. Benzylamine converts it into benzylamine hydrochloride and benzylpiperidine, $\text{C}_5\text{H}_{10}\text{Cl}_2 + 3\text{C}_7\text{H}_7\cdot\text{NH}_2 = \text{C}_5\text{H}_{10}\text{N}\cdot\text{C}_7\text{H}_7 + 2\text{C}_7\text{H}_7\cdot\text{NH}_3\cdot\text{Cl}$.

Benzoyltetrahydroquinoline reacts with phosphorus pentachloride to form the imide chloride only, a further fission being impossible. *o-γ-Chloropropylbenzanilide*, $\text{COPh}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$, forms white crystals and melts at 108°, decomposing at a higher temperature.
C. H. D.

Action of Bromine on Trichloropyrrole. Chlorobromomaleimide. VII. GIROLAMO MAZZARA and A. BORGIO (*Gazzetta*, 1904, 34, ii, 125—128. Compare *Abstr.*, 1902, i, 820; 1903, i, 51, 274; this vol., i, 614, 770, 771).—*Chlorobromomaleimide*,

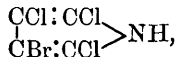


prepared by the action of bromine on an acetic acid solution of trichloropyrrole, separates from benzene in pale, lemon-yellow prisms melting at 196°. In aqueous solution, it yields a white, crystalline precipitate with ammoniacal silver nitrate solution.

On comparing the melting points of the halogen derivatives of maleimide and methylmaleimide, it is found that the mono-haloid derivatives of maleimide melt at about 50° higher than the corresponding compounds of methylmaleimide, whilst in the case of the dihaloid derivatives the difference in melting point is about 100°.

T. H. P.

Action of Sulphuryl Chloride and Bromine on Pyrrole.
 VIII. GIROLAMO MAZZARA (*Gazzetta*, 1904, 34, ii, 178—184. Compare preceding abstract).—*Trichloromonobromopyrrole*,

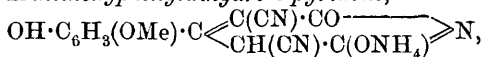


prepared by the action of bromine and sulphuryl chloride on an ethereal solution of pyrrole at 0°, separates from light petroleum in colourless, monoclinic prisms which have a yellowish-red reflex; it begins to turn brown at 105° and melts and decomposes at 115°. It has the normal molecular weight in freezing benzene. Oxidation with fuming nitric acid or bromine yields chlorobromomaleimide.

T. H. P.

Condensation of Ethyl Cyanoacetate with some Dihydroxyphenolic Aldehydes. II. GALEAZZO PICCININI (*Atti R. Accad. Torino*, 1903—1904, 39, 1024—1045. Compare this vol., i, 91 and 504).—With protocatechualdehyde, vanillin, and veratraldehyde, condensation with ethyl cyanoacetate and ammonia yields γ -substituted dicyanoglutaconimides [dicyanodihydropyridones], although in smaller proportions than in the other cases examined. The ammonium salt obtained with protocatechualdehyde is formed in two modifications, but their isomeric relations have not been determined.

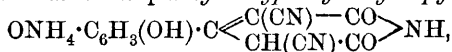
The condensation of ethyl cyanoacetate with vanillin in presence of ammonia yields: (1) the ammonium salt of 3:5-dicyano-2-hydroxy-4-p-hydroxy-m-methoxyphenyldihydro-6-pyridone,



which crystallises from water in colourless flocculi containing $2\frac{1}{2}\text{H}_2\text{O}$, of which $1\frac{1}{2}$ mols. are lost in a vacuum over sulphuric acid; it begins to turn brown at 250°, but does not melt at 300°; when suspended in water in presence of bromine vapour, it gives a red coloration which, on adding a little ammonia solution, turns green, this gradually changing back to the red. (2) p-Hydroxy-m-methoxybenzylidenecyanoacetamide, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CH}:\text{C}(\text{CN})\cdot\text{CO}\cdot\text{NH}_2$, which separates from 60 per cent. alcohol in yellow crystals melting at 210—210.5°; it remains unchanged on boiling with milk of magnesia, but yields ammonia when treated with cold lime-water; when boiled with excess of barium hydroxide, it yields vanillin, malonic acid, and ammonia, thus: $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CH}:\text{C}(\text{CN})\cdot\text{CO}\cdot\text{NH}_2 + 4\text{H}_2\text{O} = \text{OMe}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CHO} + \text{CH}_2(\text{CO}_2\text{H})_2 + 2\text{NH}_3$.

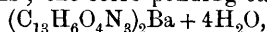
The above ammonium salt and unsaturated amide are formed in the condensation of cyanoacetamide with vanillin in presence of ammonia.

The condensation of ethyl cyanoacetate with protocatechualdehyde in presence of ammonia yields: (1) The ammonium derivative of 3:5-dicyano-2:6-diketo-4-m-p-dihydroxyphenyldihydropyridine,

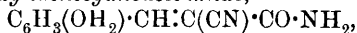


which is formed in two modifications. The α -salt (+ H_2O), obtained in small proportion, crystallises from water in tufts of minute, colourless needles. Decomposition of the corresponding lead salt with

sulphuric acid yields the free compound, which separates from water in silky, white crystals ($+2\text{H}_2\text{O}$), turning brown at 250° but not melting at 300° . The β -salt ($+\text{H}_2\text{O}$), which constitutes the main bulk of the ammonium derivative, crystallises from water in slender, but rather heavy, prisms; the corresponding *barium* salt,

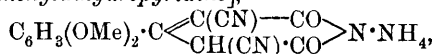


crystallises from aqueous solution in silky, white needles. (2) 3:4-Dihydroxybenzylidenecyanoacetamide,

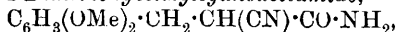


which separates from water or alcohol in intensely yellow, shining prisms, commencing to turn brown at 210° and melting and decomposing at 232° . Its aqueous solution has an acid reaction to litmus, colours ferric chloride green and alkaline hydroxides red, and reduces ammoniacal silver nitrate solution. This compound is formed without the above ammonium derivative when protocatechualdehyde is condensed with cyanoacetamide and ammonia.

The condensation of ethyl cyanoacetate with veratraldehyde in presence of ammonia yields: (1) the ammonium derivative of γ -dimethoxyphenyl $\beta\beta'$ -dicyanoglutaconimide [3:5-dicyano-2:6-diketo-4-m-p-dimethoxyphenyldihydropyridine],



which crystallises (with $2\frac{1}{2}\text{H}_2\text{O}$) from 70 per cent. alcohol in shining, white prisms; it begins to turn brown at 280 — 290° , but does not melt even at 300° . It is slightly soluble in alcohol, and its aqueous solution has an acid reaction to litmus. (2) *Ethyl* 3:4-dimethoxyphenyl-acyanoacrylate, $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{CH}:\text{C}(\text{CN}) \cdot \text{CO}_2\text{Et}$, which crystallises from 90 per cent. alcohol in long, white needles showing blue fluorescence and melting at 156° ; it is readily soluble in alcohol, acetone, benzene, and chloroform, and has the normal molecular weight in boiling acetone. (3) 3:4-Dimethoxybenzylcyanoacetamide,

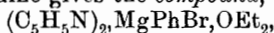


crystallises from water in very slender needles, forming an almost gelatinous mass and melting at 173° ; it is readily soluble in alcohol, and on being powdered becomes markedly electrified. T. H. P.

Combination of Mixed Organo-magnesium Compounds with the Pyridine and Quinoline Bases. BERNARDO ODDO (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 100—106).—While primary and secondary amines react with mixed organo-magnesium compounds yielding hydrocarbons (for instance, magnesium ethyl iodide gives ethane), tertiary bases such as dimethylaniline do not react with these mixed compounds (Meunier, *Abstr.*, 1903, i, 544). The author finds that the pyridine and quinoline bases react with organo-magnesium compounds yielding theoretical amounts of additive compounds, usually of the formula $(\text{R})_2\text{I} \cdot \text{Mg} \cdot \text{ROEt}_2$, where R represents the base. These substances, which may be employed to purify Grignard's compounds (*Abstr.*, 1901, i, 263), exhibit the behaviour typical of the organo-magnesium derivatives.

The action of pyridine on magnesium methyl iodide in ethereal solution yields the unstable compound, $(\text{C}_5\text{H}_5\text{N})_2\text{MgMe} \cdot \text{I} \cdot \text{OEt}_2$,

which is slightly soluble in ether, from which it is deposited as a fine powder; it reacts immediately with water, yielding methane; with benzaldehyde, it yields phenylmethylcarbinol, styrene, and polymerides of the last-named hydrocarbon. With magnesium phenyl bromide in ethereal solution, pyridine gives the *compound*,

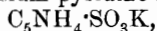


which undergoes change in the air, is very slightly soluble in ether, and reacts with water, yielding benzene.

Quinoline and magnesium methyl iodide in ethereal solution yield the *compound*, $(\text{C}_9\text{H}_7\text{N})_2, \text{MgMeI}, \text{OEt}_2$, which readily alters in the air. With magnesium phenyl bromide in ether, quinoline gives the *compound*, $(\text{C}_9\text{H}_7\text{N})_2, \text{MgPhBr}$. T. H. P.

Potassium and Sodium Salt of Pyridine-3-sulphonic Acid.

ERNST MURMANN (*Chem. Centr.*, 1904, ii, 454; from *Oesterr. Chem. Zeit.*, 7, 272—273).—Potassium pyridine-3-sulphonate,

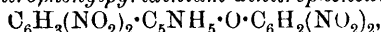


crystallises from a hot aqueous solution in pointed needles, and the sodium salt, $\text{C}_5\text{NH}_4 \cdot \text{SO}_3\text{Na}, 1\frac{1}{2}\text{H}_2\text{O}$, in large, rectangular plates. Both salts are slightly yellow and readily soluble in water; the latter loses its water of crystallisation completely at 130° . E. W. W.

*iso*Pyrophthalone. ALEXANDER EIBNER and K. HOFMANN (*Ber.*, 1904, 37, 3023—3026. Compare *Abstr.*, 1903, i, 644).—Von Huber's *isopyrophthalone* (*Abstr.*, 1903, i, 576) is identical with Jacobsen and Reimer's pyrophthalone (*Abstr.*, 1884, 335), which melts at 283° . G. Y.

Dinitrophenylpyridinium Chloride and its Products of Change. THEODOR ZINCKE, G. HEUSER, and W. MÖLLER (*Annalen*, 1904, 333, 296—345. Compare this vol., i, 448).—2 : 4-Dinitrophenylpyridinium chloride, $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{C}_5\text{NH}_5\text{Cl}$, is prepared by heating a mixture of 1-chloro-2 : 4-dinitrobenzene with excess of pyridine on the water-bath; when solution is complete, the reaction sets in with development of heat; the salt crystallises in colourless needles, which decompose into its constituents at 200° . The same decomposition takes place when the salt is heated with dilute hydrochloric acid under pressure at 180 — 185° , but when heated with water at 150 — 160° dinitrophenol and pyridine are formed. The *platini-chloride*, $[\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{C}_5\text{NH}_5]_2\text{PtCl}_6$, crystallises in yellow needles melting and decomposing at 221° . The corresponding *bromide* is prepared from 1-bromo-2 : 4-dinitrobenzene and pyridine, and forms pale yellow needles melting and decomposing into its constituents at 225° . The *perbromide*, $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{C}_5\text{NH}_5 \cdot \text{Br}_3$, is obtained by the action of bromine water on either the chloride or bromide, and crystallises in orange-yellow needles melting at 162 — 163° . The *periodide* crystallises in dark violet, lustrous needles melting at 125° . The *dichromate*, $[\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{C}_5\text{NH}_5]_2\text{Cr}_2\text{O}_7$, prepared from the chloride and aqueous potassium dichromate, crystallises in orange-yellow prisms melting and decomposing at 114 — 115° . In the foregoing decomposition of the

chloride by water, in addition to the formation of dinitrophenol and pyridine, *dinitrophenylpyridinium dinitrophenoxide*,



is also produced by union of the unchanged pyridinium base with the phenol; it crystallises in yellow needles melting at 142—143°.

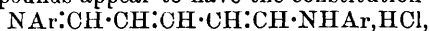
Under the influence of alkali hydroxides or ammonia, the pyridinium chloride is converted into a *red* compound, which is probably represented by one of the formulæ: $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{N}:\text{CH}:\text{CH}:\text{CH}:\text{CH}:\text{CH}:\text{OH}$ or $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{NH}:\text{CH}:\text{CH}:\text{CH}:\text{CH}:\text{CHO}$; this compound is prepared most readily by treatment of the pyridinium compound with aqueous sodium carbonate until the original dirty-brown precipitate has become dark red and crystalline; from acetone, it forms deep red, rhombic crystals, which melt and decompose with elimination of pyridine at 180°, and is dissolved by alkalis with a dark violet coloration, slowly disappearing as the substance decomposes. When treated with hydrogen chloride in the absence of water, the original pyridinium salt is regenerated, but aqueous hydrogen chloride converts it into dinitroaniline; primary and secondary bases effect also the latter decomposition, but phenylhydrazine causes the elimination of water.

Attempts to convert the pyridine residue into some stable substance by oxidation failed; chromic acid in acetic acid solution leads to the formation of dinitroaniline and carbon dioxide; alkaline permanganate behaves in a similar manner, and nitric acid acts with extreme violence.

Attempts to prepare a methiodide were unsuccessful; when heated with methyl iodide and methyl alcohol at 100°, only dinitroaniline was produced. When boiled with alcohol, the ethyl ether of dinitrophenol and pyridine are formed, together with a small quantity of a substance crystallising in brownish-red leaflets, which dissolves in acetic acid with a deep red coloration.

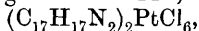
The action of halogens on the red substance was tried in the hope of obtaining stable and characteristic additive products of the group $\text{C}_5\text{H}_6\text{O}_2$; additive compounds were formed, but they could not be isolated.

Primary aromatic amines react with dinitrophenylpyridinium chloride according to the equation: $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{C}_5\text{NH}_5\text{Cl} + 2\text{NH}_2\text{Ar} = \text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{NH}_2 + \text{C}_5\text{H}_7\text{N}_2\text{Ar}_2\text{Cl}$. The compound, which is produced together with the dinitroaniline, is the *hydrochloride* of a mono-acid base; it is intensely coloured and can be converted into the base. These compounds can be obtained from the red product, formed from the pyridinium chloride by the action of alkali, by treatment with the aromatic amine and subsequent addition of hydrogen chloride. Although certain substituted anilines can bring about this decomposition, 2:4-dichloroaniline and the three nitroanilines are unable to do so. These compounds appear to have the constitution



and have the character of dyes, most being coloured intensely red, but some existing also in a bluish-violet modification. The red form is obtained from dilute alcohol, whilst the violet form is obtained on drying or on crystallising from absolute alcohol or acetone. In some cases, these two forms are dimorphous, but in others are due to the presence of water or alcohol of crystallisation.

The *hydrochloride* of the dianilide, $\text{NPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{NHPh}$, is prepared from aniline and the pyridinium chloride, and crystallises in dark red needles melting at $143\text{--}144^\circ$; the *platinichloride*,



is a reddish-brown, crystalline powder melting and decomposing at $179\text{--}180^\circ$. The *hydrobromide* forms red, lustrous needles, becoming violet on drying and melting at 167° . The *base* crystallises in yellow leaflets or brownish-red needles, which decompose slowly on keeping and melt and decompose at $85\text{--}86^\circ$.

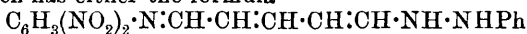
The *hydrochloride* of di-*p*-chlorodianilide, $\text{C}_{17}\text{H}_{14}\text{N}_2\text{Cl}_2\cdot\text{HCl}$, crystallises in reddish- or bluish-violet needles melting and decomposing at 143° ; the free *base* crystallises in yellow or reddish-brown needles or in hydrated, yellow needles melting and decomposing at $108\text{--}110^\circ$, and, although it decomposes on keeping, is more stable than the unsubstituted base. When heated with acetic anhydride, *p*-chloroacetanilide and an *acetyl* derivative, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{OAc}$, which crystallises in colourless needles or plates melting at 129° , are produced.

The *hydrochloride* of the di-*m*-chlorodianilide, $\text{C}_{17}\text{H}_{14}\text{N}_2\text{Cl}_2\cdot\text{HCl}$, crystallises in steel-blue or red needles melting and decomposing at $135\text{--}136^\circ$; the free *base* forms yellow, lustrous leaflets or reddish-brown needles melting at 109° .

The *hydrochloride* of the di-*p*-toluidide, $\text{C}_{17}\text{H}_{14}\text{N}_2\text{Me}_2\cdot\text{HCl}$, prepared as the compounds just described, crystallises in slender, red needles or in dark red, rhombic plates, or in forms which are bluish-violet by reflected light and garnet-red by transmitted light; it melts at $142\text{--}143^\circ$. The free *base* crystallises in golden plates or red needles melting and decomposing at 121° . The *hydrochloride* of the di-*o*-toluidide is more soluble than that of the para-compound, and crystallises in leaflets or plates melting and decomposing at 148° . The free *base* is oily and unstable.

The *hydrochloride* of the di-*as*-xylidide, $\text{C}_{17}\text{H}_{12}\text{N}_2\text{Me}_4\cdot\text{HCl}$, crystallises in pale red leaflets melting and decomposing at 145° ; the free *base* is an oil. The *hydrochloride* of the di- ψ -cumidide, $\text{C}_{17}\text{H}_{10}\text{N}_2\text{Me}_6\cdot\text{HCl}$, crystallises in dark red or violet needles melting and decomposing at 134° or in lustrous, red plates melting at $144\text{--}145^\circ$. The free *base* crystallises in golden leaflets or red needles melting and decomposing at 93° .

The action of phenylhydrazine on dinitrophenylpyridinium chloride is represented by the equation: $\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{C}_5\text{NH}_5\text{Cl} + \text{N}_2\text{H}_5\text{Ph} = \text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{C}_5\text{NH}_5\cdot\text{N}_2\text{H}_5\text{Ph} + \text{HCl}$; the pyridine ring is broken, as in the case of alkalis and aliphatic amines. The phenylhydrazine compound, which has either the formula



or the formula $\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{NH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{N}\cdot\text{NHPh}$, crystallises in black, lustrous needles melting and decomposing at 140° .

The dianilides under a variety of conditions can be converted into quaternary pyridinium bases, the pyridine ring being again regenerated: $\text{NAr}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{NHAr}, \text{HCl} = \text{NH}_2\text{Ar} + \text{C}_5\text{NH}_5\text{ArCl}$. The reaction takes place very readily when the salt is heated with hydrochloric acid, or when the hydrochloride is melted, or by heating

the salt with arylamines. The method of preparation last mentioned permits of these bases being prepared directly from the dinitrophenylpyridinium chloride, which is for this purpose heated in alcoholic solution with excess of amine. The pyridinium base is separated from the amine by precipitating with mercuric chloride, which forms an insoluble compound with the former.

Phenylpyridinium chloride, $C_5NH_5PhCl \cdot H_2O$, forms colourless, monoclinic crystals, which are hygroscopic in moist air and melt at $105-106^\circ$. The *picrate* crystallises in needles melting at $123-124^\circ$; the *platinichloride*, $(C_5NH_5PhCl)_2PtCl_4$, crystallises in orange-red needles melting and decomposing at $202-203^\circ$. The *dichromate* crystallises in dark yellow needles melting at $162-163^\circ$ and decomposing at 180° .

p-Chlorophenylpyridinium chloride, $C_5NH_5Cl \cdot C_6H_4Cl$, crystallises in colourless prisms or needles melting at $123-124^\circ$; from the aqueous solutions of this salt, alkali hydroxides precipitate a brownish-red solid melting at $201-202^\circ$; the *picrate* crystallises in pale yellow needles melting at $143-144^\circ$; the *platinichloride* crystallises in orange-red needles melting and decomposing at $222-223^\circ$, and the *dichromate* in orange, six-sided leaflets melting at $192-193^\circ$ and then exploding.

o-Chlorophenylpyridinium chloride, $C_5NH_5Cl \cdot C_6H_4Cl \cdot H_2O$, prepared by heating the dinitro-compound with *o*-chloroaniline on the water-bath, crystallises in concentric groups of needles or leaflets melting at $88-93^\circ$; the *picrate* crystallises in yellow needles melting at $104-105^\circ$, the *platinichloride* in orange-red needles melting at $204-205^\circ$, and the *dichromate* in yellow needles melting and decomposing at 111° .

The dianilides are decomposed by bromine; thus, the compound from aniline and the dinitro-compound yields *s*-tribromoaniline (m. p. 118°) and *s*-tribromophenylpyridinium *perbromide*, $C_5NH_5Br \cdot C_6H_2Br_3 \cdot Br_2$, which crystallises in yellow leaflets melting and decomposing at $212-214^\circ$. When the latter is warmed with acetone, *s*-tribromophenylpyridinium *bromide* is formed, crystallising in white needles melting and decomposing at $310-312^\circ$; the *dichromate* forms yellow crystals melting and decomposing at 160° .

The *p*-chlorodianilide behaves in a similar manner; 2:6-dibromo-4-chloroaniline (m. p. 95°) and the *perbromide* of 2:6-dibromo-4-chlorophenylpyridinium *bromide*, $C_5NH_5Br \cdot C_6H_2ClBr_2 \cdot Br_2$, are formed; the latter, which crystallises in golden-yellow leaflets melting and decomposing at $217-219^\circ$, is converted by warming with acetone into the *bromide*, $C_5NH_5Br \cdot C_6H_2ClBr_2$, which crystallises in white needles melting and decomposing at $270-271^\circ$ and is reconverted into the *perbromide* by treatment with bromine. The *platinichloride* melts and decomposes at $266-268^\circ$, and the *dichromate*, which forms yellow crystals, at 151° .

The author discusses the constitution of the dyes described in the foregoing, concludes that they are identical with the compounds obtained by König by the action of amines on bromocyanopyridine (this vol., i, 449), and agrees with König as to the constitution of these substances.

K. J. P. O.

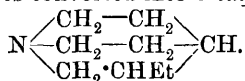
Behaviour of Tertiary Amines towards Organo-magnesium Compounds. FRANZ SACHS and LUDWIG SACHS (*Ber.*, 1904, 37, 3088—3092).—Quinoline combines with magnesium phenyl bromide dissolved in absolute ether to form a greyish-white additive compound, $C_9H_7N, MgPhBr$, which is sparingly soluble in ether; the nitrogen atom is here probably quinquivalent, as water readily decomposes the compound giving quinoline. That the substance does not contain magnesium phenyl bromide as such is shown by the fact that the latter cannot be detected by means of Michler's ketone. If the substance were formed by addition to a double linking of the nucleus, decomposition by water would give a dihydroquinoline and not quinoline as is actually the case.

The additive compound, $C_9H_7N, MgEtBr$, is less stable than the analogous phenyl derivative; it is decomposed by alcohol giving ethane. W. A. D.

A New So called L-Reaction. LUDWIG PAUL (*Chem. Zeit.*, 1904, 28, 702—703).—When an aniline salt is heated with glycerol at 215° for an hour, a base, "AL," which perhaps is a tetrahydroquinoline derivative, $C_6H_4 \begin{smallmatrix} CH_2 \cdot CH \\ \backslash \quad / \\ NH \cdot CH \cdot C_6H_4 \cdot NH_2 \end{smallmatrix}$, is obtained; it is easily diazotised and coupled with phenols. Similar compounds are obtained by heating glycerol with the hydrochlorides of sulphanilic acid, α -naphthylamine, *p*-phenylenediamine, *p*-aminoacetanilide, *p*-nitroaniline, and dimethylaniline. No analyses are given of any of the products. W. A. D.

Some New Dyes. LUDWIG PAUL (*Chem. Zeit.*, 1904, 28, 703—704).—A detailed account of the interaction of glycerol with dimethylaniline and with *m*-phenylenediamine (compare preceding abstract). No analyses are given of the products nor are formulæ ascribed to them. W. A. D.

β -Ethylquinuclidine. WILLIAM KOENIGS (*Ber.*, 1904, 37, 3244—3252).—On heating methylhexahydro- β -collidine, $OH \cdot C_9H_{18}N$, for some hours with fuming hydriodic acid and phosphorus, a compound, $C_9H_{18}NI, HI$, is formed, which when crystallised from alcohol is colourless, melts and decomposes at 233° , and on cautious treatment with sodium hydroxide is converted into 3-ethylquinuclidine,



This is a colourless oil with an odour similar to collidine, boiling at 190 — 192° under 720 mm. pressure, has a molecular weight of 139° and forms a series of well-defined salts. The *picrate* crystallises in bright yellow flat needles melting at 153 — 154.5° ; the *hydrochloride* is colourless and melts at 208 — 211° ; the *aurichloride* forms golden, glistening plates, which melt at 176 — 178° ; the *platinichloride* melts and decomposes at 221° , and the *mercurichloride* crystallises in colourless prisms easily soluble in water. 3-Ethylquinuclidine does not react with per-

manganate or naphthalenesulphonic chloride. The *methiodide* crystallises from chloroform in colourless plates melting at 55—80°, but possibly still contains some of the solvent; the *methochloride*, which is very hygroscopic, forms a sparingly soluble, reddish-yellow *platinichloride*, melting and decomposing at 265°, and also an *aurichloride* melting at 187°.

The ethyl cincholeuponate derived by Skraup from one of the cinchonine alkaloids gives on reduction with sodium and alcohol a base forming a crystalline *aurichloride*, $C_9H_{19}ON, HAuCl_4$, which melts at 90—99°. This base, when heated with hydriodic acid and phosphorus, forms a compound $C_9H_{18}NI, HI$, melting at 138—139°, which, after a time, is converted into a base, $C_9H_{17}N$, of which the derivatives very closely resemble those of β -ethylquinuclidine; the hydriodide melts at 227—230°, the hydrochloride at 210—212°, the picrate at 153—155°, the platinichloride at 223° (under decomposition), and the aurichloride at 176—177°. A 0.5 gram solution of the hydrochloride in 6 c.c. of water shows an optical rotation $\alpha_D + 5^\circ$ in a 1 dm. tube. The base thus appears to be an optically active form of β -ethylquinuclidine. E. F. A.

2-Phenylquinoline. ERNST MURMANN (*Chem. Centr.*, 1904, ii, 454; from *Oesterr. Chem. Zeit.*, 7, 273).—2-Phenylquinoline boils at 363° (corr.), melts at 84°, and solidifies at 80—81°; it is very sparingly soluble in cold light petroleum or alcohol, but somewhat more soluble in hot light petroleum, and readily so in hot alcohol, benzene, ethyl acetate, amyl acetate, ether, carbon disulphide, or acetone. The base shows strong triboluminescence; even small fragments emit light when shaken violently in the dark. E. W. W.

Action of Magnesium Benzyl Chloride on Cyclaminones. HERMANN DECKER and ROBERT PSCHORR [and, in part, O. KOCH and HANS EINBECK] (*Ber.*, 1904, 37, 3396—3404. Compare this vol., i, 344, 611).—The action of magnesium benzyl chloride on 10-methyl-9-acridone leads to the formation of 9-benzylidene-10-methyl-9:10-dihydroacridine (this vol., i, 620).

1-Benzylisoquinoline methiodide, $C_{16}H_{13}N, MeI$, is obtained on addition of a concentrated aqueous solution of potassium iodide to the solution in dilute sulphuric acid of the product from the action of magnesium benzyl chloride on 2-methylisoquinoline. It crystallises in flat, yellow needles, commences to sinter at 230°, and melts and decomposes at 247—248°. With potassium hydroxide in concentrated aqueous solution, it yields a precipitate of 1-benzylidene-2-methyl-1:2-dihydroisoquinoline, the parent substance of the isopapaverine bases; this dissolves in benzene or ether to a yellow solution, and forms the colourless ammonium base with water. When heated for some time over its melting point, the methiodide loses methyl iodide and yields 1-benzylisoquinoline, which, when almost pure, boils at 211—213° under 11 mm. pressure (Rügheimer, *Abstr.*, 1900, i, 522); the *hydrochloride* crystallises in glistening needles and melts at 171—172°; the *picrate* crystallises in prisms and melts and decomposes at 184—185° (corr.); the *platinichloride* melts and decomposes at 218°. **2-Benzylquinoline methiodide**, obtained by the action of potassium iodide on the

product from the interaction of magnesium benzyl chloride and 1-methylquinolone, crystallises in long, yellow needles, decomposes when heated above 220° , and, when acted on by an alkali hydroxide yields the yellow *benzylidene* base, which does not form an ammonium base with water. In the same manner, 6:7-dimethoxy-1-benzylisoquinoline *methiodide* is prepared from magnesium benzyl chloride and 6:7-dimethoxy-2-methylisoquinolone. It crystallises in thick, yellow prisms, melts at $206-207^{\circ}$, and gives the *isopapaverine* reactions.

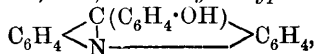
N-Methylisopapaverine (this vol., i, 338) or *N*-methylpapavarinium methyl sulphate was oxidised in alkaline aqueous solution by the passage of a current of air during 8 days. After extraction with benzene, the distillation residue was dissolved in hot hydrochloric acid, and, on cooling, dimethoxy-2-methylisoquinoline hydrochloride, $C_{12}H_{13}O_3N \cdot HCl \cdot 2H_2O$, crystallised out on cooling. It forms colourless needles and melts at $160-175^{\circ}$. The free base, $C_{12}H_{13}O_3N$, melts at $109-110^{\circ}$ (Pschorr, this vol., i, 611). The sparingly soluble *hydriodide* rapidly becomes brown on exposure to air; the yellow, crystalline *picrate* melts at $136-137^{\circ}$. *Dimethoxy-2-ethylisoquinolone hydrochloride*, obtained in the manner as the 2-methyl salt, contains $2H_2O$ and melts and decomposes at $142-150^{\circ}$; the *base* melts at $60-62^{\circ}$.

The methyl ether of vanillin (veratraldehyde), which melts at $42-43^{\circ}$, is obtained as a product of the oxidation of *N*-methylisopapaverine (compare this vol., i, 339). Veratric acid and probably veratryl alcohol are also formed by the prolonged action of the alkali hydroxide. The oxidation of the *isopapaverinium* bases can be carried out also with potassium ferricyanide or permanganate.

Veratryl alcohol, $OH \cdot CH_2 \cdot C_6H_3(OMe)_2$ [1:3:4], formed along with veratric acid by the action of warm concentrated sodium hydroxide solution on veratraldehyde, is a viscid, colourless oil which boils at $172-173^{\circ}$ under 14 mm., or at $296-297^{\circ}$ under 732 mm. pressure, and gives a red coloration with concentrated sulphuric acid. *Veratryl chloride*, $CH_2Cl \cdot C_6H_3(OMe)_2$, formed by the action of hydrogen chloride on the alcohol in benzene solution, crystallises in colourless needles and melts at $50-51^{\circ}$. The *chloride* and the *bromide*, obtained in the same manner, yield the alcohol when treated with cold water. G. Y.

Preparation of Acridinium Dyes. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 152662).—On heating acridinium compounds or their leuco-compounds with concentrated sulphuric acid and 2 or 3 mols. of formaldehyde in open vessels, orange-red dyes are obtained, consisting partly of acridine compounds, but chiefly of acridinium derivatives. The two classes may be separated by means of ammonia. The products are not identical with those obtained by heating acridine-yellow, &c., with formaldehyde and dilute hydrochloric acid under pressure (D.R.-P. 135771). C. H. D.

Researches in the Phenylacridine Group. EDMOND LANDAUER (*Bull. Soc. chim.*, 1904, [iii], 31, 1083—1094. Compare Bernthsen, *Abstr.*, 1883, 580, 1099, 1133, and 1884, 1356, 1357; and Hess and Bernthsen, *Abstr.*, 1885, 800).—5-o *Hydroxyphenylacridine*,



is best prepared by mixing diphenylamine (1 mol.) with dry salicylic acid (1.5 mols.) and zinc chloride (3 mols.) and heating for five hours at 170—175°, the mixture being well stirred throughout the operation. When cold, the mass is extracted with alcohol and the solution poured into excess of water; the precipitate is washed successively with water, ammonia solution, and light petroleum, and finally recrystallised from alcohol. The substance crystallises in greenish-yellow, microscopic prisms and melts and decomposes at 289—290° (corr.). It is soluble in solutions of the alkali hydroxides and in acids (the solution in sulphuric acid is fluorescent), but is only slightly soluble in organic liquids and insoluble in water.

5-Di-m-phenylacridinyl ether, prepared from diphenylamine and *m*-hydroxybenzoic acid, separates from boiling aniline in yellow, monoclinic crystals and may be purified by sublimation at 325° under 20 mm. pressure and then melts and decomposes at 366—367°. Ebullioscopic determinations of the molecular weight give anomalous results. It is readily soluble in aniline, nitrobenzene, and quinoline, but is insoluble or nearly so in most other organic solvents and water. The solution in sulphuric acid fluoresces green. The *salts* are sparingly soluble in water and acids; the *platinichloride* forms fine, reddish-yellow, monoclinic crystals, and the *aurichloride*, golden-yellow crystals; the *picrate*, fine yellow needles or elongated prisms, and melts at 245°. When the ether is heated with ethyl iodide in closed tubes at 180° to 185° for seven hours, the *diethiodide* is obtained; this forms brownish-black crystals, is soluble in alcohol, melts at 208—209°, and is converted by warming with a solution of potassium hydroxide into a yellow *substance*, which melts and decomposes at 359—360°. With acetic anhydride, the *acetate* of the ether is produced.

5-p-Hydroxyphenylacridine, prepared by the method already described, using *p*-hydroxybenzoic acid, forms yellow, monoclinic crystals, and melts and decomposes at 355—356°. It is soluble in aniline, naphthalene, boiling diphenylamine, and in alkalis, less so in alcohols, and insoluble in water. The solution in sulphuric acid fluoresces strongly green, that in hydrochloric acid is similarly, but less vividly, fluorescent. The *dichromate* forms yellowish-red needles, the *picrate*, slender, yellow needles, the *platinichloride*, reddish-yellow crystals, and the *aurichloride*, yellow, monoclinic crystals. *Sodium 5-p-hydroxyphenylacridinesulphonate*, prepared in the usual manner, forms crystalline scales with a pink tint; it is readily soluble in the usual solvents.

Solutions of these three compounds in acetic acid possess no tinctorial power, whereas the solutions in mineral acids dye wool, cotton, silk, and leather in yellow tints. Since the introduction of the hydroxyl group into the 5-phenyl nucleus of phenylacridine gives rise to dyes, it appears likely that the amino-group would behave similarly, although Hess and Bernthsen (*loc. cit.*) state that 5-*p*-aminophenylacridine has no tinctorial power.

T. A. H.

Transformation of *o*-Nitro- and *o-p*-Dinitrobenzyl Chlorides into Acridine Derivatives. CARLO BAEZNER (*Ber.*, 1904, 37, 3077—3083).—Instead of using *o*-aminobenzyl alcohol in the synthesis

of 1:2-phenonaphthacridine from β -naphthol (Ullmann and Baezner, Abstr., 1902, i, 694), the author heats *o*-nitrobenzyl chloride with stannous chloride, β -naphthol, and hydrochloric acid in alcoholic solution. 1:2-Phenonaphthacridine nitrate forms yellow crystals melting at 217°, and the hydrochloride crystallises from alcohol. β -Naphthylamine or phenyl- β -naphthylamine can be substituted for β -naphthol in the condensation.

5-Hydroxy-1:2-phenonaphthacridine, $C_6H_4 \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} C_{10}H_5 \cdot OH$, prepared similarly from 2:7-dihydroxynaphthalene and *o*-nitrobenzyl alcohol or *o*-nitrobenzyl chloride, crystallises from nitrobenzene in yellowish-brown needles having a bronze-like lustre and melts at 322°; the hydrochloride forms red crystals and the methochloride crystallises from alcohol in red needles.

9-Amino-1:2-phenonaphthacridine, $NH_2 \cdot C_6H_3 \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} C_{10}H_6$, prepared from 2:4-dinitrobenzyl chloride and β -naphthol, crystallises from toluene or dilute alcohol in yellow needles and melts at 270°. The hydrochloride forms red crystals and the picrate yellowish-red needles.
W. A. D.

A New Formation of Naphthacridines. [Phenonaphthacridines]. FRITZ ULLMANN and ANTONIO LA TORRE (*Ber.*, 1904, 37, 2922—2928. Compare Abstr., 1902, i, 119).—*o*-Tolyl- α -naphthylamine (Friedländer, Abstr., 1884, 79) is best prepared by fusing α -naphthol with *o*-toluidine hydrochloride. Lead oxide converts it into 2:1-phenonaphthacridine, $\begin{smallmatrix} \text{CH} \cdot \text{CH} \cdot \text{C} \cdot \text{CH} \cdot \text{C} \cdot \text{CH} \cdot \text{CH} \cdot \text{C} \cdot \text{CH} \cdot \text{CH} \\ | \quad | \quad | \quad | \quad | \quad | \quad | \quad | \\ \text{CH} \cdot \text{CH} \cdot \text{C} \cdot \text{N} - \text{C} = \text{C} = \text{C} \cdot \text{CH} \cdot \text{CH} \end{smallmatrix}$, crystallising from benzene and light petroleum in long, glistening needles and melting at 108°. The picrate separates from nitrobenzene in small, yellow crystals and melts and decomposes at 226—229°. The hydrochloride forms yellow needles and sinters at 241°, and melts and decomposes at 244°. The alcoholic solution is yellow with bluish-green fluorescence. The nitrate forms yellow leaflets and melts and decomposes at 188—189°. The methiodide, $C_{18}H_{14}NI$, prepared by warming the base with methyl sulphate, and precipitating the aqueous solution with potassium iodide, crystallises from alcohol in orange needles, melts at 262—263°, and dissolves in hot alcohol to a yellow solution with bluish-green fluorescence. Alkali hydroxides precipitate the yellow, crystalline carbinol-base from the aqueous solution.

2:1-Phenonaphthacridine is identical with Pictet and Erlich's α -chrysidine (Abstr., 1891, 216).

1:2-Phenonaphthacridine, prepared by heating *o*-tolyl- β -naphthylamine with sulphur or lead oxide, melts at 131° and is identical with the product from *o*-aminobenzyl alcohol (Ullmann and Baezner, Abstr., 1902, i, 694) and with Pictet and Erlich's β -chrysidine. The picrate forms needles and sinters at 255°, and melts and decomposes at 260°. The hydrochloride forms long, yellow needles; the nitrate forms yellow needles, and melts and decomposes at 217°. The methiodide forms orange, felted needles, becoming orange-red on heating and melting

at 264°, and dissolves sparingly in hot water to a yellow solution with slight green fluorescence.

The melting points found are considerably higher than those obtained by Pictet and Erlich.

12-Methyl-1:2-phenonaphthacridol, $C_{18}H_{15}ON$, prepared by addition of ammonia to a solution of the methiodide, separates from benzene in small, slightly pink, glistening crystals, becoming red at 160°, brown at 190°, sintering at 195°, and melting at 206–207°. The solutions in alcohol, ether, or toluene are colourless, with blue fluorescence, that in acetic acid is yellow with bluish-green fluorescence.

C. H. D.

Constitution of Quinophthalone. Alkali Derivatives of Quinophthalone and of isoQuinophthalone. ALEXANDER EIBNER and H. MERKEL (*Ber.*, 1904, 37, 3006–3011. Compare Abstr., 1901, i, 348; 1902, i, 494, 644).—When dissolved in absolute ethyl alcohol and treated with sodium ethoxide, quinophthalone yields the sodium derivative, $C_{18}H_{10}O_2NNa$, which is obtained as a scarlet powder, consisting of sheaves of microscopic needles. This sodium derivative is obtained also by the action of sodium hydroxide on quinophthalone in benzene or chloroform solution, or, with evolution of hydrogen, by the action of sodium on quinophthalone in dry benzene or xylene solution, or by treatment of isoquinophthalone (Abstr., 1902, i, 644) with sodium ethoxide in absolute alcoholic solution. The potassium derivative, $C_{18}H_{10}O_2NK$, obtained by the action of potassium ethoxide on quinophthalone, forms orange-coloured, microscopic, slender needles. These alkali derivatives yield quinophthalone when treated with water, or when repeatedly washed with 96 per cent. alcohol. They have probably the constitution $C_6H_4 \begin{smallmatrix} \diagup CO \diagdown \\ \diagdown C(OM) \diagup \end{smallmatrix} C \cdot C_9H_6N$ (compare Gabriel, Abstr., 1893, i, 415).

G. Y.

isoQuinophthalone. ALEXANDER EIBNER and K. HOFMANN (*Ber.*, 1904, 37, 3011–3018. Compare Abstr., 1902, i, 644).—When boiled with aqueous alkali hydroxides, isoquinophthalone slowly dissolves to a yellow solution, which, on addition of acetic acid, yields a yellow, flocculent precipitate. The product, *quinolyacetophenone-o-carboxylic acid*, $C_9H_6N \cdot CH_2 \cdot CO \cdot C_6H_4 \cdot CO_2H$, separates from its solution in acetone, on addition of water, in yellow, prismatic crystals, melts and decomposes at 155°, is easily soluble in chloroform, benzene, or acetone, and in aqueous alkali hydroxides or carbonates, or mineral acids. The aqueous solutions of the alkali salts give precipitates with the salts of the heavy metals. The *oxime*, $C_{18}H_{13}O_2N:NOH$, crystallises in matted needles, melts and decomposes at 145°, is easily soluble in aqueous alkali hydroxides, and yields ammonia and quinaldine when heated with soda-lime. With phenylhydrazine, the acid yields

a *phthalazone*, $C_9H_6N \cdot CH_2 \cdot C \begin{smallmatrix} \diagup C_6H_4 \cdot CO \\ \diagdown N - NPh \end{smallmatrix}$, which crystallises in white, matted needles, melts at 102–105°, yields fluorescein when heated with resorcinol and zinc chloride, and evolves quinaldine when heated with soda-lime. When acted on by sodium nitrite and dilute hydrochloric

acid, the acid yields an isonitroso-derivative, $C_{13}H_{12}O_4N_2$, which crystallises in colourless, slender needles, and melts and decomposes, with formation of quinophthalone, at 205° . The action of benzenediazonium chloride on the acid, dissolved in aqueous sodium hydroxide, leads to the formation of a red precipitate of *quinolyformazyl*, $NHPh \cdot N:C(C_6NH_6) \cdot N:NPh$, which crystallises in reddish-brown needles, melts and decomposes at 185° , and dissolves in hot dilute hydrochloric acid to a red, in concentrated sulphuric to a blue, solution, which changes to orange-red on dilution. It yields quinaldine when heated with soda-lime, aniline, phenylhydrazine, and quinaldine when reduced with zinc and hydrochloric acid.

Quinolyacetophenone-*o*-carboxylic acid is converted into quinophthalone when heated above its melting point, or when warmed with concentrated sulphuric acid, the product being precipitated on addition of water, and when heated with benzaldehyde.

The following homologues of *isoquinophthalone* have been obtained by heating the corresponding quinaldine with phthalic anhydride. 8-*Methylisoquinophthalone*, from 2:8-dimethylquinoline, crystallises in yellow needles and melts at 235° ; 6-*methylisoquinophthalone*, from 2:6-dimethylquinoline, crystallises in yellow needles and melts at 237° ; 6:8-*dimethylisoquinophthalone*, from 2:6:8-trimethylquinoline, crystallises in yellow needles and melts at 231° ; 5:6:8-*trimethylisoquinophthalone*, from 2:5:6:8-tetramethylquinoline, forms yellow needles and melts at 236° ; β -*naphthaisoquinophthalone*, from β -naphthol-2-methylquinoline, crystallises in yellow needles and melts at 273° . These *isoquinophthalones* are less highly coloured, and usually melt at a lower temperature than the corresponding quinophthalones, into which they are converted by means of sodium ethoxide. They give the characteristic red formazyl derivative with benzenediazonium chloride and alkali.

G. Y.

Quinophthalone, *iso*Quinophthalone, and Quinophthaline. ALEXANDER EIBNER and K. HOFMANN (*Ber.*, 1904, 37, 3018—3023. Compare *Abstr.*, 1901, i, 348).—When heated with excess of phenylhydrazine, quinophthaloneanil is converted into *quinophthalonephenylhydrazone*, $C_{18}H_{11}ON:N_2HPh$, which crystallises in dark red needles and thin plates, melts at 206° , gives Bülow's reaction, and is hydrolysed by concentrated hydrochloric acid at 210° , with formation of quinophthalone and *p*-phenylenediamine.

With bromine in chloroform solution, *isoquinophthalone* forms a scarlet, crystalline *perbromide*, which is converted by sulphurous acid into a yellow bromine compound, by ammonia into *isoquinophthalone*. The filtrate from the *perbromide* deposits salmon-coloured needles which are a mixture of the *perbromide* and the monobromo-compound (compare *Abstr.*, 1902, i, 644). With a limited quantity of bromine, *isoquinophthalone* yields a *monobromo*-derivative, $C_{18}H_{10}O_2NBr$, which crystallises in yellow needles, commences to lose bromine at 170° , melts at 275° , and yields *isoquinophthalone* when treated with dilute ammonia.

The action of bromine on β -quinophthaline in chloroform solution leads to the formation of a dark red *perbromide*, which loses the whole

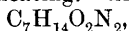
of its bromine on treatment with sulphurous acid or ammonia, and a *tetrabromo*-derivative, which crystallises in colourless prisms, melts at 78° , and must have the constitution $C_9H_6N \cdot CBr_2 \cdot CBr < \begin{smallmatrix} C_6H_4 \\ NBr \end{smallmatrix} > CO$.

When boiled with sodium hydroxide solution, tetrabromo- β -quinophthaline dissolves to a golden-yellow solution, which gives the quinolyacetophenonecarboxylic acid reaction with benzenediazonium chloride.

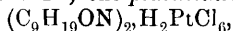
In future, quinophthalone and α -quinophthaline are to be termed *s*-quinophthalone and *s*-quinophthaline; the *iso*-series will be termed *as*-quinophthalone and *as*-quinophthaline. G. Y.

Derivatives of Diacetonealkamines. II. MORITZ KOHN (*Monatsh.*, 1904, 25, 817—849. Compare this vol., i, 378).—The action of formaldehyde on diacetonealkamine [methyl- β -aminoisobutylcarbinol] leads to the formation of 4:4:6-*trimethyltetrahydro*-1:3-

oxazine, $O < \begin{smallmatrix} CH_2-NH \\ CHMe \cdot CH_2 \end{smallmatrix} > CMe_2$, which is a mobile liquid with an intense basic odour, boils at $149-152^\circ$, is easily soluble in ether, and absorbs moisture and carbon dioxide. The *hydrochloride* is a viscous syrup; the *aurichloride*, $C_7H_{15}ON, HAuCl_4$, melts at $140-143^\circ$; the *platinichloride* forms glistening needles; the crystalline *picrate*, $C_7H_{15}ON, C_6H_3O_7N_3$, melts at 118° or at 131° after sintering at 124° , depending on the manner of heating. The *nitroso*-derivative,

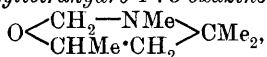


is a mobile liquid with an aromatic odour and boils at $129-131^\circ$ under 22—24 mm. pressure. The *acetyl* derivative, $C_7H_{14}ONAc$, is a colourless liquid, boils at $123-125^\circ$ under 19 mm. and at $235-237^\circ$ under atmospheric pressure; its *aurichloride*, $C_9H_{17}O_2N, HAuCl_4$, is crystalline. The action of methyl iodide on the base in methyl alcoholic solution leads to the formation of the *methiodide* of the methylated base, which, with silver chloride, yields the *methochloride* as a syrup, crystallising after some weeks; the *aurichloride*, $C_9H_{19}ON, HAuCl_4$, melts and decomposes at 241° ; the *platinichloride*,

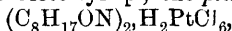


forms a yellowish-red, crystalline precipitate and melts and decomposes at 255° .

3:4:4:6-*Tetramethyltetrahydro*-1:3-*oxazine*,



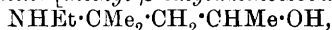
boils at $166-168^\circ$ and mixes with water with development of heat; the *hydrochloride* is a colourless syrup; the *platinichloride*,



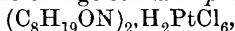
forms a sandy, glistening, crystalline powder; the *aurichloride*, $C_8H_{17}ON, HAuCl_4$, crystallises in glistening leaflets, commences to soften at 80° , melts almost completely at 120° , and is liquid at 136° ; the *picrate* crystallises in slender needles and melts at $171-173^\circ$. With methyl iodide, the base yields the same *methiodide* as is obtained from the secondary base. With ethyl iodide, the tertiary base forms the *ethiodide*; when treated successively with silver and gold chlorides, it yields the *aurichloride*, $C_{10}H_{21}ON, HAuCl_4$, which crystallises in

slender needles, commences to decompose at 175° , and melts at 204° ; the *platinichloride*, $(C_{10}H_{21}ON)_2 \cdot H_2PtCl_6$, forms an orange-yellow, crystalline precipitate and melts at 230° .

Ethyl diacetonalalkamine [*methyl- β -ethylaminoisobutylcarbinol*],



obtained by reduction of ethyl diacetonalamine, prepared from mesityl oxide and ethylamine, is a colourless liquid with an ammoniacal odour, boiling at $189-191^{\circ}$; the orange-coloured *platinichloride*,

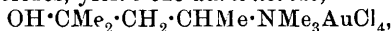


is sparingly soluble in water. 3-Ethyl-4 : 4 : 6-trimethyltetrahydro-1 : 3-

oxazine, $O \begin{array}{c} \text{CH}_2 - \text{NEt} \\ \diagup \quad \diagdown \\ \text{CHMe} \cdot \text{CH}_2 \end{array} CMe_2$, formed by the action of formalde-

hyde on ethyl diacetonalalkamine, boils at $176-180^{\circ}$; the *hydrochloride* is a viscid, colourless syrup; the *aurichloride*, $C_9H_{19}ON \cdot HAuCl_4$, crystallises in long needles and melts at $180-182^{\circ}$; the *platinichloride* crystallises in glistening prisms; the crystalline picrate melts at $112-115^{\circ}$. With methyl iodide, the base yields the same quaternary iodide as is obtained by the action of ethyl iodide on the tetramethyl base.

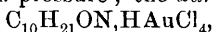
The action of methyl iodide on β -aminoisohexylcarbinol leads to the formation of a quaternary *iodide*, which, on successive treatment with silver and gold chlorides, yields the *aurichloride*,



which crystallises in glistening needles and melts at $106-108^{\circ}$; the *platinichloride*, $(C_9H_{22}ON)_2 \cdot PtCl_6$, crystallises in leaflets and melts at 105° .
G. Y.

Derivatives of Diacetonalalkamines. III. MORITZ KOHN (*Monatsh.*, 1904, 25, 850-864).—4:4:6-Trimethyl-2-isopropyltetrahydro-

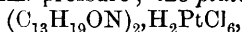
1 : 3-oxazine, $O \begin{array}{c} \text{CHPr}^a \cdot \text{NH} \\ \diagup \quad \diagdown \\ \text{CHMe} \cdot \text{CH}_2 \end{array} CMe_2$, obtained by treating diacetonalalkamine with isobutaldehyde, is a clear, mobile liquid and boils at $171-173^{\circ}$ under 744 mm. pressure; the *aurichloride*,



crystallises in needles and melts and decomposes at 144° ; the *platinichloride*, $(C_{10}H_{21}ON)_2 \cdot H_2PtCl_6$, crystallises from the concentrated solution. The *nitroso*-derivative, $C_{10}H_{20}O_2N_2$, is a yellow oil, which appears to decompose when distilled in a vacuum or in a current of steam.

3 : 4 : 4 : 6-Tetramethyl-2-isopropyltetrahydro-1 : 3-oxazine, obtained from methyl diacetonalalkamine and isobutaldehyde, distils at $190-194^{\circ}$ under 750 mm. pressure; the *aurichloride*, $C_{11}H_{23}ON \cdot HAuCl_4$, crystallises in long, thin needles and melts and decomposes at 140° ; the *platinichloride* crystallises in plates and leaflets. With methyl iodide, the base forms a *methiodide* which is converted by silver chloride into the *methochloride*; the *aurichloride*, $C_{11}H_{23}ONMe \cdot AuCl_4$, melts at $123-126^{\circ}$.

2-Phenyl-4 : 4 : 6-trimethyltetrahydro-1 : 3-oxazine, obtained from diacetonalalkamine and benzaldehyde, is a viscid, colourless oil which boils at 131° under 10 mm. pressure; the *platinichloride*,



crystallises in thick plates; the precipitate obtained on addition of gold chloride to the solution of the hydrochloride contained less gold than required by the formula $C_{13}H_{19}ON, HAuCl_4$. The *nitroso*-derivative, $C_{13}H_{18}O_2N_2$, crystallises in thin, white plates and melts at $108-111^\circ$.

2-Phenyl-3:4:4:6-tetramethyltetrahydro-1:3-oxazine, obtained from methyl diacetonealkamine and benzaldehyde, is a yellow, mobile oil, which boils at $267-270^\circ$ under 747 mm. pressure; the *aurichloride*, $C_{14}H_{21}ON, HAuCl_4$, crystallises in thin needles and melts and decomposes at $164-167^\circ$; the *platinichloride*, $(C_{14}H_{21}ON)_2 \cdot H_2PtCl_6$, forms glistening prisms. G. Y.

Oxazine Derivatives of Anthraquinone. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 153517).—3-Halogen-1-arylamino-2-hydroxyanthraquinones, prepared by replacing the 1-halogen atom in 1:3-dibromoxanthopurpurin, tetrabromoanthraflavic acid, tetrabromoanthrachrysone, &c., by arylamino-residues, are converted into oxazine derivatives by removal of hydrogen haloid on heating alone or with organic or inorganic bases. Or the process may be completed in one operation, a bromohydroxyanthraquinone, for instance, being heated with an aromatic amine.

3-Bromo-1-p-toluidino-2:4-dihydroxyanthraquinone, from 1:3-dibromoxanthopurpurin and *p*-toluidine, dissolves in concentrated sulphuric acid to a yellow solution, and in sodium hydroxide to a blue solution, and yields an oxazine on heating with heavy petroleum, sodium acetate, or a mixture of sodium acetate with acetic acid or aniline. C. H. D.

Connection between the Fluorescence and Chemical Constitution of Derivatives of Benzoxazole. FERDINAND HENRICH and GUSTAV OPFERMANN (*Ber.*, 1904, 37, 3108—3111).—It has previously been shown (*Abstr.*, 1899, i, 171) that 5-hydroxy-1-phenyl-

3-methylbenzoxazole,
$$\begin{array}{c} \text{CH:CMc:C:N} \\ \text{OH:C=CH-C-O} \end{array} \gg \text{CPh}$$
, when dissolved in

concentrated sulphuric acid, is strongly fluorescent, whereas 3-hydroxy-5-methylbenzoxazole and its 1-methyl derivative are not so. That the fluorescence is not due merely to the magnitude of the radicle in position 1 is now shown by the fact that 5-hydroxy-3-methyl-1-hexylbenzoxazole is also not fluorescent; this substance, prepared by condensing *o*-amino-*o*-cinol with heptoyl chloride, crystallises from light petroleum in yellowish-white needles and melts at 99° .

The 5-benzoyl and 5-methyl derivatives of 5-hydroxy-1-phenyl-3-methylbenzoxazole are also not fluorescent, and the same is true of 3-hydroxy-1-phenyl-5-methylbenzoxazole.

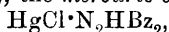
5-Methoxy-1-phenyl-3-methylbenzoxazole, prepared by methylating the hydroxy-compound, crystallises from dilute alcohol in needles and melts at 98° . *3-Hydroxy-1-phenyl-5-methylbenzoxazole*, prepared by condensing 3:5-dihydroxy-*p*-toluidine with benzoyl chloride, crystallises from light petroleum and melts at $124-126^\circ$.

3-Hydroxy-1-phenylbenzoxazole, prepared from 2-aminoresorcinol, crystallises from benzene in nodular aggregates and melts at $138-139^\circ$. W. A. D.

Oxidation Products from *p*-Phenylenediamine. II. ERNST ERDMANN (*Ber.*, 1904, 37, 2906—2913. Compare this vol., i, 778).—Hydrogen peroxide oxidises *p*-phenylenediamine according to the equation: $3C_6H_8N_2 + 3H_2O_2 = C_{18}H_{18}N_6 + 6H_2O$. The base obtained, tetra-aminodiphenyl-*p*-azophenylene, crystallises in brown needles and melts at 242—243° (compare Bandrowski, *Abstr.*, 1894, i, 236, and Willstätter, this vol., i, 511). Lead peroxide forms quinonedi-imide as the principal product. The latter compound is highly poisonous.
C. H. D.

Immedial-pure-blue. II. ROBERT GNEHM and FELIX KAUFLEB (*Ber.*, 1904, 37, 3032—3033).—The tetrabromodimethylaminothiazone obtained on brominating immedial-pure-blue (this vol., i, 687) has now been prepared from Bernthsen's methylene-violet, and the identity of the two products proved by measurement of the absorption bands in various solvents.
E. F. A.

Action of Iodine and of Halogenated Substances on the Metallic Derivatives of Dibenzoylhydrazide. ROBERT STOLLÉ and ALFRED BENRATH (*J. pr. Chem.*, 1904, [ii], 70, 263—280. Compare *Abstr.*, 1900, i, 531).—The sodium derivative of *s*-dibenzoylhydrazide, N_2HNaBz_2 , crystallises in yellow needles; the mercuric derivative, $C_{14}H_{10}O_2N_2Hg$ (?), the mercuric chloride derivative,



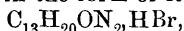
and the lead derivative, $(N_2HBz_2)_2Pb$, are obtained as white precipitates; the basic lead derivative, $OHPb \cdot N_2HBz_2$, is yellow; when heated, the silver derivative yields diphenylfurodiazole.

When treated with sulphuric acid (3 vols. of acid, 1 vol. of water), azodibenzoyl yields nitrogen, hydrazine, and benzoic acid; with sodium ethoxide in alcoholic solution, it yields nitrogen *s*-dibenzoylhydrazide and benzoic acid; with water, at the ordinary temperature for two days, and finally warmed at 60°, it forms nitrogen, tribenzoylhydrazide, and a trace of *s*-dibenzoylhydrazide. The melting point of tribenzoylhydrazide varies greatly with the rate of heating; the melting point 198° (Stollé, this vol., i, 453) was due to slow heating, and not to the existence of a second tribenzoylhydrazide; when treated with sodium ethoxide in hot alcoholic solution, it yields the sodium derivative of *s*-dibenzoylhydrazide.

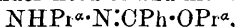
Acetyl-s-dibenzoylhydrazide, N_2HAcBz_2 , formed by the action of acetyl chloride on dibenzoylhydrazide in ethereal solution, separates from alcohol in thick, colourless crystals, melts at 169—170°, and is hydrolysed by alkali hydroxides to *s*-dibenzoylhydrazide. *Ethyl s-dibenzoylhydrazidocarboxylate*, $N_2HBz_2 \cdot CO_2Et$, formed by the action of ethyl chlorocarbonate on the silver derivative of dibenzoylhydrazide, crystallises in matted, slender needles, melts at 130°, and yields dibenzoylhydrazide on hydrolysis with alkali hydroxides. *Ethyl hydrazido-carboxylate hydrochloride*, $N_2H_3 \cdot CO_2Et, HCl$, obtained by treating hydrazine hydrate with ethyl chlorocarbonate, forms hygroscopic crystals, melts at 129°, and, with benzaldehyde, yields Thiele and Lachmann's ethyl benzylidenehydrazidocarboxylate (*Abstr.*, 1896, i, 208). Traube's ethyl dibenzoylhydrazidacetate (*Abstr.*, 1898, i,

235) is formed by the action of ethyl chloroacetate on the sodium derivative of *s*-dibenzoylhydrazide; the *silver* salt is obtained as a white precipitate; the *acid*, $N_2HBz_2 \cdot CH_2 \cdot CO_2H$, crystallises in small, flat, colourless prisms and melts and decomposes at 195° . Dibenzoylbenzylhydrazine (Curtius, Abstr., 1900, i, 611) is obtained by acting with benzyl chloride on the sodium derivative of *s*-dibenzoylhydrazide; it melts at 152° .

Dibenzoylethylhydrazine, N_2HEtBz_2 , is formed along with diphenylfurodiazole when sodio-*s*-dibenzoylhydrazide is heated with ethyl bromide in a sealed tube at 130° . It crystallises with 2 mols. of water of crystallisation, melts at 100° , or when anhydrous, at 133° . *Dibenzoyl-n-propylhydrazine*, formed by the action of *n*-propyl bromide on sodio-*s*-dibenzoylhydrazide at 140° , crystallises in flat, glistening needles and melts at 131° . It is formed from *n*-propylhydrazine hydrochloride by the Schotten-Baumann reaction (compare Abstr., 1902, i, 57). The action of *n*-propyl bromide on dibenzoylhydrazide at 160° leads to the formation of the propyl ether of *s*-benzoylpropylhydrazine. It is obtained in the form of its *hydrobromide*,



which crystallises in slender needles and melts at 209° . The *ether*,



crystallises in slender, silky needles, melts at 100° , and reduces ammoniacal silver solutions in presence of an alkali hydroxide.

G. Y.

Action of Phenylmethylhydrazine on Sugar. RUDOLF OFNER (Ber., 1904, 37, 3362—3363. Compare this vol., i, 689).—Phenylmethylosazone, prepared by the action of phenylmethylhydrazine on dextrose, melts at 153° and is identical with the product obtained by Fischer from glucosone, and by Neuberg (Abstr., 1902, i, 264, 660) from *d*-fructose. It may also be prepared from phenylmethylhydrazine and dextrose-phenylmethylhydrazone. When phenylmethylhydrazine, which has undergone partial decomposition into phenylhydrazine, is used, phenylmethylphenylglucosazone, melting at 192 — 195° , is also formed.

A. McK.

Coupling of Acid Hydrazides with Sugars. RICHARD KAHL (Zeit. Ver. Deut. Zucker-Ind., 1904, 1091—1119).—By the action of various acid hydrazides on sugars of the aldose type, the author has been enabled to prepare derivatives of these sugars which are insoluble or sparingly soluble in most solvents, and from which the original sugars may readily be obtained.

Dextrose-p-bromobenzoylhydrazone, $C_6H_{12}O_5 \cdot N \cdot NH \cdot CO \cdot C_6H_4Br$, prepared from dextrose and *p*-bromobenzoylhydrazide best in acetic acid solution, is insoluble in all the ordinary solvents, but extremely soluble in pyridine, from which ether precipitates it in white flocks; it has no true melting point, but chars at 200 — 202° when slowly heated, or at 206 — 207° when the heating is rapid. When gently heated with dilute sulphuric acid, it yields hydrazine sulphate, dextrose, and *p*-bromobenzoic acid, the last of which separates out almost completely in the solid state. The dextrose may also be recovered by

boiling the *p*-bromobenzhydrazide in water with a slight excess of benzaldehyde. Dextrose cannot be estimated by means of this compound, the highest yield of which was found to be 80 per cent.

No *p*-bromobenzhydrazide derivatives of lævulose, sucrose, maltose, and lactose could be prepared. The formation of the *p*-bromobenzhydrazone can hence be employed as a means of detection of an aldose in presence of large quantities of ketoses or bioses.

l-Arabinose-*p*-bromobenzoylhydrazone, $C_5H_{10}O_4 \cdot N \cdot NH \cdot CO \cdot C_6H_4Br$, forms a crystalline precipitate insoluble in all ordinary solvents, slightly soluble in cold pyridine, and more so on heating. When rapidly heated, it decomposes at 215—216°. It is decomposed by boiling water in presence of benzaldehyde, yielding a solution from which the arabinose can be crystallised.

Xylose-p-bromobenzoylhydrazone is insoluble in all solvents except pyridine, which resolves it into its constituents. It decomposes at 258—260°.

d-Mannose-*p*-bromobenzoylhydrazone, $C_6H_{12}O_5 \cdot N \cdot NH \cdot CO \cdot C_6H_4Br$, separates in microscopic, flat prisms, which are insoluble in the ordinary solvents, slightly soluble in pyridine in the cold, and extremely so in the hot, part of the compound being thus decomposed. It is readily resolved into its components by boiling water and decomposes at 205° when rapidly heated.

d-Galactose-*p*-bromobenzoylhydrazone, $C_6H_{12}O_5 \cdot N \cdot NH \cdot CO \cdot C_6H_4Br$, forms hard, microscopic prisms insoluble in the ordinary solvents and decomposed by pyridine. It is readily resolved by boiling water and decomposes at 216°.

p-Chlorobenzoylhydrazone, $C_6H_4Cl \cdot CO \cdot NH \cdot NH_2$, prepared by the action of hydrazine on ethyl *p*-chlorobenzoate in aqueous-alcoholic solution, separates from water as a felted mass of fine needles melting at 163°. It dissolves readily in alcohol, and reduces ammoniacal silver solution in the cold and Fehling's solution on boiling.

Dextrose-p-chlorobenzoylhydrazone, $C_6H_{12}O_5 \cdot N \cdot NH \cdot CO \cdot C_6H_4Cl$, prepared by the interaction of dextrose and *p*-chlorobenzoylhydrazide in alcoholic solution, is insoluble in the ordinary solvents and is decomposed by boiling with alcohol; on heating, it decomposes at 211°.

l-Arabinose-*p*-chlorobenzoylhydrazone, $C_5H_{10}O_4 \cdot N \cdot NH \cdot CO \cdot C_6H_4Cl$, is slowly dissolved and decomposed by boiling alcohol or cold pyridine; its decomposition temperature is 203°.

Salicylhydrazide, $OH \cdot C_6H_4 \cdot CO \cdot NH \cdot NH_2$, prepared by the action of hydrazine hydrate on ethyl salicylate in alcoholic solution, separates from aqueous solution in long prisms, which dissolve slightly in ether and more readily in benzene, alcohol, or acetic acid, and melt at 147°; it reduces ammoniacal silver solution in the cold and Fehling's solution on heating.

Dextrosesalicylhydrazone, $C_6H_{12}O_5 \cdot N \cdot NH \cdot CO \cdot C_6H_4 \cdot OH$, is extremely insoluble and readily decomposable; on heating, it decomposes at 198°.

l-Arabinosesalicylhydrazone, $C_5H_{10}O_4 \cdot N \cdot NH \cdot CO \cdot C_6H_4 \cdot OH$, crystallises in microscopic prisms decomposing at 191°; cold water or boiling alcohol gradually decomposes it.

Gallic hydrazide, $C_6H_2(OH)_3 \cdot CO \cdot NH \cdot NH_2$, obtained by the interaction of ethyl gallate and hydrazine hydrate, forms a crystalline powder which reduces ammoniacal silver solutions in the cold and Fehling's solution on heating, and decomposes at $295-298^\circ$. On account of its great insolubility, its sugar derivatives could not be prepared.

Dextrose- β -naphthylsulphonhydrazone, $C_6H_{12}O_5 \cdot N \cdot NH \cdot SO_2 \cdot C_{10}H_7$, forms a white, sandy precipitate consisting of microscopic prisms; boiling water rapidly and completely converts it into dextrose and the hydrazone.

l-Arabinose- β -naphthylsulphonhydrazone, $C_5H_{10}O_4 \cdot N \cdot NH \cdot SO_2 \cdot C_{10}H_7$, forms a white powder which decomposes at 175° and dissolves to a slight extent in hot alcohol.

Owing to the extremely slight solubilities and ready preparation of the two preceding compounds, the use of β -naphthylsulphonhydrazide for the isolation of dextrose and arabinose is especially recommended.

Attempts to prepare compounds of dextrose with the hydrazides of palmitic, phenylacetic, and phenylpropionic acids were unsuccessful.

Rhamnoseseemicarbazone, $C_6H_{12}O_4 \cdot N \cdot NH \cdot CO \cdot NH_2$, crystallises from aqueous alcohol in glassy, microscopic prisms decomposing at $169-170^\circ$; it is soluble in water and slightly so in alcohol. It is resolved into its components by boiling water in presence of benzaldehyde.

d-Galactoseseemicarbazone, $C_6H_{12}O_5 \cdot N \cdot NH \cdot CO \cdot NH_2$, is deposited from aqueous alcohol in flat, glassy prisms decomposing at $186-189^\circ$; it is moderately soluble in water and slightly so in alcohol.

d-Mannoseseemicarbazone, $C_6H_{12}O_5 \cdot N \cdot NH \cdot CO \cdot NH_2$, crystallises from aqueous alcohol in clear, hygroscopic, microscopic prisms and is soluble in water and very slightly so in alcohol.

Semicarbazide does not react with sugars of the ketose type, as is shown by observing the rotatory power of the solutions at intervals extending over a long period of time.

T. H. P.

Synthesis of a Piperazine Derivative by the Polymerisation of Chloroethylamine and Decomposition of the Quaternary Salts of Piperazine by Alkalis. LUDWIG KNORR (*Ber.*, 1904, 37, 3507—3519).—*Dimethylchloroethylamine*, $NMe_2 \cdot C_2H_4Cl$, prepared by heating dimethylethanolamine with fuming hydrochloric acid at $170-180^\circ$, decomposing the hydrochloride formed with concentrated potassium hydroxide, and extracting with ether, forms a clear oil boiling at $109-110^\circ$. The *hydrochloride* crystallises from alcohol in large prisms and darkens and melts at 201° ; the *aurichloride* forms long prisms and melts at 140° , previously sintering. Boiling alkali hydroxides decompose the base into dimethylethanolamine and tetramethylethylenediamine, acetylene being evolved: $4NMe_2 \cdot C_2H_4Cl \rightarrow NMe_2 \cdot C_2H_4 \cdot NMe_2 + C_2H_2 + 2NMe_2 \cdot C_2H_4 \cdot OH$. The salts of tetramethylethylenediamine have been described by Freund (*Abstr.*, 1897, i, 495); the base forms a volatile oil, boiling at $120-122^\circ$ under 745 mm. pressure.

The oily dimethylchloroethylamine polymerises rapidly, yielding a white, neutral, crystalline mass of *N*-dimethylpiperazine dimetho-

chloride, $2\text{NMe}_2 \cdot \text{C}_2\text{H}_4\text{Cl} = \text{NMe}_2\text{Cl} \left\langle \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \right\rangle \text{NMe}_2\text{Cl}$ (compare Gabriel, Abstr., 1896, i, 121; Marckwald and Frobenius, Abstr., 1902, i, 22). The same product is obtained by heating together tetramethylethylenediamine and ethylene chloride in alcoholic solution, and by decomposing synthetical 1:4-dimethylpiperazine dimethiodide with silver oxide and evaporating with hydrochloric acid. It decomposes above 300° into methyl chloride and 1:4-dimethylpiperazine. The *platinichloride* crystallises from boiling water in slender, orange needles and decomposes at 270° ; the *aurichloride* forms golden leaflets and decomposes at 220° ; the *picrate* forms insoluble, yellow crystals and decomposes at about 280° ; the *ferrocyanide* forms a white, crystalline precipitate.

1:4-Dimethylpiperazine, prepared by distilling the above methochloride or by methylating piperazine by means of potassium methyl sulphate, boils at $131\text{--}132^\circ$ under 752 mm. pressure (compare Schmidt and Wichmann, Abstr., 1892, i, 210).

Boiling alkali hydroxides decompose 1:4-dimethylpiperazine dimethochloride into tetramethylethylenediamine and dimethylethanolamine. The latter products are therefore not derived directly from dimethylchloroethylamine in the experiments described above, but from the piperazine derivative formed as an intermediate product. C. H. D.

Aminopyrazoles. LUDWIG KNORR (*Ber.*, 1904, 37, 3520—3525).—4-Aminopyrazole is readily prepared by reducing nitropyrazole with zinc dust and acetic acid (compare Wollers and Behrend, Abstr., 1902, i, 843). The *picrate* melts at $193\text{--}194^\circ$ and contains 2 mols. of picric acid; the *picrolonate* melts at 242° and contains only 1 mol. of picrolonic acid. The *base* may be obtained by evaporation in an atmosphere of hydrogen, or by adding sodium hydroxide to a solution of a salt covered with a layer of ethyl acetate in an atmosphere of hydrogen, and may be sublimed in hydrogen, forming snow-white crystals melting at $80\text{--}82^\circ$. It is very hygroscopic, and dissolves in water to a neutral solution, which only darkens slowly in the air. Alkaline solutions readily absorb oxygen.

4-Aminopyrazole forms very stable diazonium salts, which are not decomposed by boiling water and form azo-dyes in the normal manner. Warm potassium iodide solution converts them into 4-iodopyrazole.

[With H. PEMSEL].—3-(or 5)-Aminopyrazole may be prepared from pyrazole-3-(5)-carboxylic acid by successive conversion into the ethyl ester, hydrazide, azoimide, and urethane. These compounds will be described elsewhere. 3-(5)-Aminopyrazole forms a colourless, viscous, hygroscopic oil, boiling at 282° under 753 mm. pressure or at 218° under 122 mm., and dissolving readily in water, alcohol, or ethyl acetate, sparingly in ether. The aqueous solution is neutral; very little oxidation takes place in alkaline solution. The diazonium salts resemble those of 4-aminopyrazole.

[With PAUL MORENTZ].—3:5-Diaminopyrazole, prepared in a similar manner from pyrazole-3:5-dicarboxylic acid (Abstr., 1894, i, 543),

forms a yellow, uncrystallisable syrup, readily soluble in water or alcohol, insoluble in ether. Nitrous acid forms diazonium compounds. Boiling dilute acids or alkalis decompose the base.

The *dibenzoyl* derivative melts at 207—208°, previously sintering.

All three amino-bases reduce solutions of gold salts. C. H. D.

5-Chloro-4-amino-1-phenyl-3-methylpyrazole. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 153861).—Zinc dust and sodium hydroxide reduce 5-chloro-1-phenyl-3-methylpyrazole-4-azobenzene to 1-phenyl-3-methylpyrazole-4-azobenzene (Michaelis and Leonhardt, this vol., i, 124). Acid reducing agents, however, reduce the azo-group without removing the chlorine, forming 5-chloro-4-amino-1-phenyl-3-methylpyrazole, which crystallises from light petroleum in tablets, melts at 49°, and dissolves readily in alcohol or ether. The *hydrochloride* crystallises from alcohol in tablets, decomposes at 220°, and yields a diazonium compound with nitrous acid.

Methylating agents and an alkali hydroxide form phenyldimethyl-dimethylaminopyrazolone.

1-Phenyl-3-methylpyrazolone-4-azo-o-toluene, from diazotised o-toluidine and phenylmethylpyrazole, forms red needles and melts at 183°. Phosphorus oxychloride at 100° converts it into 5-chloro-1-phenyl-3-methylpyrazole-4-azo-o-toluene, crystallising in orange needles and melting at 97°.

Similar compounds may be prepared from p-phenetidine. 1-Phenyl-2-methylpyrazolone-4-azo-p-phenetole forms orange needles and melts at 159°. 5-Chloro-1-phenyl-2-methylpyrazole-4-azo-p-phenetole forms orange leaflets and melts at 123°. C. H. D.

1-Phenyl-3:4:5-trimethylpyrazole. JAMES MCCONNAN (*Ber.*, 1904, 37, 3525—3528).—The properties of 1-phenyl-3:4:5-trimethylpyrazole given by Knorr and Jochheim (*Abstr.*, 1903, i, 528) differ considerably from those given by Posner (*Abstr.*, 1902, i, 83). The values found by the author for the boiling point of the base, the melting points of the picrate and aurichloride, and the decomposing point of the platinichloride are identical with those obtained by Knorr and Jochheim. The hydrochloride melts at about 90°, and the *picrolonate* decomposes at 120°. Posner's phenyltrimethylpyrazole probably contained some phenyldimethylpyrazole.

C. H. D.

Pyrimidines : 4 : 6-Diamino-2-oxypyrimidine. HENRY L. WHEELER and GEORGE S. JAMIESON (*Amer. Chem. J.*, 1904, 32, 342—357).—2-Methylthiol-4:6-dioxypyrimidine (2-methylthiolbarbituric acid), $\text{NH} \begin{array}{c} \text{C}(\text{SMe})\text{:N} \\ \text{CO} \text{---} \text{CH}_2 \end{array} \text{CO}$, obtained by the action of methyl iodide on thiobarbituric acid in presence of sodium ethoxide, crystallises in needles, is sparingly soluble in hot water and less so in alcohol, does not melt below 300°, but gradually assumes a pale brown colour. When this substance is heated with phosphorus pentachloride or oxychloride, it is converted into 4:6-dichloro-2-methylthiolpyrimidine, $\text{N} \begin{array}{c} \text{C}(\text{SMe})\text{:N} \\ \text{CCl} \text{---} \text{CH} \end{array} \text{CCl}$, which boils at 135—136° under 14 mm. pressure,

crystallises in prisms, melts at 41—42°, and is readily soluble in ether, alcohol, or light petroleum.

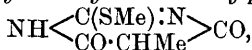
4-Chloro-6-amino-2-methylthiopyrimidine, $\text{N} \begin{smallmatrix} \text{C(SMe)}=\text{N} \\ \text{C(NH}_2\text{)}\cdot\text{CH} \end{smallmatrix} \text{CCl}$, obtained by heating 4 : 6-dichloro-2-methylthiopyrimidine with alcoholic ammonia for 4 hours at 125—126° in a sealed tube, crystallises in colourless needles, melts at 127—128°, and is sparingly soluble in water; when this substance is heated with alcoholic ammonia in a sealed tube for 2 hours at 185—190° and 4 hours at 215—220°, it is converted into 2 : 4 : 6-triaminopyrimidine (Gabriel, Abstr., 1902, i, 59). By the action of concentrated hydrochloric acid on 4-chloro-6-amino-2-methylthiopyrimidine, 4-chloro-6-amino-2-oxypyrimidine (4-chlorocytosine), $\text{N} \begin{smallmatrix} \text{CO}=\text{NH} \\ \text{C(NH}_2\text{)}\cdot\text{CH} \end{smallmatrix} \text{CCl}$, is produced, which crystallises from hot water in aggregates of small, slender prisms and does not melt at 300° but sinters and gradually becomes red; when this compound is heated with alcoholic ammonia, a substance is produced which forms small crystals, does not melt below 307°, is sparingly soluble in water, and contains 24.9 per cent. of nitrogen and no chlorine.

4 : 6-Diamino-2-methylthiopyrimidine, $\text{N} \begin{smallmatrix} \text{C(SMe)}=\text{N} \\ \text{C(NH}_2\text{)}\cdot\text{CH} \end{smallmatrix} \text{C}\cdot\text{NH}_2$, prepared by the action of methyl iodide on 4 : 6-diamino-2-thiopyrimidine, crystallises from hot water in slender prisms and melts and decomposes at 185—186°. When this substance is heated with concentrated hydrochloric acid, methyl mercaptan is evolved, and 4 : 6-diamino-2-oxypyrimidine, $\text{NH} \begin{smallmatrix} \text{CO}=\text{N} \\ \text{C(NH}_2\text{)}\cdot\text{CH} \end{smallmatrix} \text{C}\cdot\text{NH}_2$, is produced, which crystallises in slender, rectangular prisms, is sparingly soluble in hot water, becomes yellow at 297° and remains unmelted at 347°; its hydrochloride and picrate are described. If the treatment with hot hydrochloric acid is continued after the whole of the mercaptan has been expelled, the 4 : 6-diamino-2-oxypyrimidine is completely converted into barbituric acid. This diamino-oxypyrimidine is not identical with the base obtained by Kutscher from the nucleic acid of yeast (Abstr., 1903, i, 668), which is probably 5 : 6-diamino-2-oxypyrimidine.

5-isoNitroso-4 : 6-dioxy-2-methylthiopyrimidine (2-methylthiolvioluric acid), $\text{NH} \begin{smallmatrix} \text{C(SMe)}=\text{N} \\ \text{CO}\cdot\text{C(NOH)} \end{smallmatrix} \text{CO}$, obtained by the action of nitrous acid on 2-methylthiol-4 : 6-dioxypyrimidine, crystallises with 2H₂O in red, flat, pointed prisms. When this substance is reduced with ammonium sulphide, 5-amino-4 : 6-dioxy-2-methylthiopyrimidine (2-methylthiouramil), $\text{NH} \begin{smallmatrix} \text{C(SMe)}=\text{N} \\ \text{CO}\cdot\text{CH(NH}_2\text{)} \end{smallmatrix} \text{CO}$, is produced, which becomes brown at 285°, remains unmelted at 301°, and is sparingly soluble in water or hydrochloric acid.

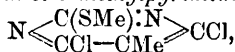
2-Thio-4 : 6-dioxy-5-methylpyrimidine (2-thio-5-methylbarbituric acid), $\text{NH} \begin{smallmatrix} \text{CS}=\text{NH} \\ \text{CO}\cdot\text{CHMe} \end{smallmatrix} \text{CO}$, prepared by heating ethyl methylmalonate with thiocarbamide in presence of sodium ethoxide, forms thin plates

and melts and decomposes at about 244° ; the compound crystallises with $1\text{H}_2\text{O}$, which is evolved at 120° . 2-Thio-4:6-dioxy-5-ethylpyrimidine (2-thio-5-ethylbarbituric acid) crystallises from water in long, acicular prisms, melts at $190\text{--}191^{\circ}$, and is soluble in alcohol. When an alcoholic solution of 2-methylthiolbarbituric acid is heated with methyl iodide, 4:6-dioxy-2-methylthiol-5-methylpyrimidine,

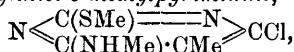


is produced, which crystallises from acetic acid in short prisms, decomposes at about 303° , and is almost insoluble in water or alcohol. 4:6-Dioxy-2-methylthiol-5-ethylpyrimidine crystallises from acetic acid, melts and decomposes at about 257° , and is readily soluble in alcohol and sparingly so in water.

4:6-Dichloro-2-methylthiol-5-methylpyrimidine,



obtained by the action of phosphorus pentachloride on 4:6-dioxy-2-methylthiol-5-methylpyrimidine, boils at $153\text{--}154^{\circ}$ under 18 mm. pressure, crystallises in stout, colourless prisms, and melts at 64° ; when warmed with sodium ethoxide, it is converted into 4-chloro-6-ethoxy-2-methylthiol-5-methylpyrimidine, $\text{N} \begin{array}{c} \text{C(SMe)=N} \\ \text{C(OEt)\cdot CMe} \end{array} \text{CCl}$, which crystallises from alcohol in colourless prisms, melts at 85° , and is readily soluble in alcohol or benzene, but insoluble in water. 4-Chloro-6-methylamino-2-methylthiol-5-methylpyrimidine,



obtained by heating 4:6-dichloro-2-methylthiol-5-methylpyrimidine with an alcoholic solution of methylamine, crystallises from alcohol in thick prisms and melts at 157° .

5-Dimethylaminouracil, $\text{NH} \begin{array}{c} \text{CO}\text{---}\text{NH} \\ \text{CO}\cdot\text{C(NMe}_2\text{)} \end{array} \text{CH}$, prepared by the action of dimethylamine on 5-bromouracil, crystallises from water in small, thin, colourless plates and melts and decomposes at about 297° .

5-Methylamino-4-methyluracil, $\text{NH} \begin{array}{c} \text{CO}\text{---}\text{NH} \\ \text{CO}\cdot\text{C(NHMe)} \end{array} \text{CMe}$, obtained by heating 5-bromo-4-methyluracil with aqueous methylamine, crystallises in colourless prisms with $1\text{H}_2\text{O}$ and melts at 214° ; its hydrochloride melts and decomposes at 273° .

2-Methylthiol-4:6-dimethylpyrimidine, $\text{N} \begin{array}{c} \text{C(SMe)\cdot N} \\ \text{CMe=CH} \end{array} \text{CMe}$, prepared by the condensation of acetylacetone with the methyl iodide additive compound of thiocarbamide in presence of potassium hydroxide, boils at $135\text{--}137^{\circ}$ under 28–29 mm. pressure, melts at $23\text{--}24^{\circ}$, and is fairly soluble in water; another substance is produced in this reaction, which crystallises from alcohol in colourless, rectangular prisms and melts at $153\text{--}154^{\circ}$. 4:6-Dimethyl-2-oxypyrimidine melts at $198\text{--}199^{\circ}$ (compare Evans, Abstr., 1902, i, 111). E. G.

Behaviour of the Group $\text{N}\cdot\text{C}\cdot\text{N}$ towards Acylating Agents. GUSTAV HELLER [and A. KÜHN] (*Ber.*, 1904, 37, 3112–3119).—On

adding benzoyl chloride to a solution of glyoxaline in pyridine, the glyoxaline ring is broken, dibenzoyldiaminoethylene being formed; with benzoic acid and sodium benzoate, glyoxaline gives only the benzoate, $C_{10}H_{10}O_2N_2$, which crystallises from ether and melts at 99° .

Benziminazole and β -naphthiminazole with benzoyl chloride in pyridine solution readily give the corresponding benzoyl derivatives; but when benziminazole is heated with acetic anhydride and sodium acetate, *o*-diacetylaminobenzene is obtained.

Diphenylformamidine, when acetylated according to Liebermann's method, gives only acetanilide; on benzylation in benzene solution, *diphenylformamidine dibenzoate*, $C_{27}H_{24}O_4N_2$, melting at 177 – 178° , is the sole product.

Di-*p*-toluidinomethane is readily acetylated or benzoylated; the *dibenzoyl* derivative, $CH_2(NBz \cdot C_6H_4Me)_2$, is comparatively unstable, and on being heated with dilute hydrochloric acid gives principally benzo-*p*-toluidide. *Dibenzoyldi-p-phenetidylmethane* melts at 83 – 84° .

Dihydro-orexine (phenyltetrahydroquinazoline), when mixed with benzoyl chloride in pyridine, gives *o*-benzoylaminobenzylaniline, $NHBz \cdot C_6H_4 \cdot CH_2 \cdot NPh$, and a small quantity of dibenzoylaminobenzylaniline. On acetylation, dihydro-orexine gives a product which does not crystallise.

Carbodi-*p*-tolylimide, on benzylation, gives the additive compound *benzoyldi-p-tolylcarbamide*, $C_{22}H_{20}O_2N_2$, which crystallises from acetone and melts at 152 – 153° ; some di-*p*-tolylcarbamide, melting at 260° , is also formed. On acetylation by Liebermann's method, acetyldi-*p*-tolylcarbamide is obtained; it melts at 148° , not at 140° as stated by Bamberger and Destraz (Abstr., 1902, i, 538).

Orexine (phenyldihydroquinazoline), on benzylation in pyridine solution, gives an additive compound, *1-benzoyl-2-benzoxyl-3-phenyl-tetrahydroquinazoline*, $C_6H_4 \begin{matrix} \swarrow NBz \cdot CH \cdot OBz \\ \searrow CH_2 \cdot NPh \end{matrix}$; it crystallises from alcohol or benzene in nodular aggregates of needles, melts at 168 – 169° , and on being heated with alcoholic potassium hydroxide gives a substance crystallising from benzene and melting at 116 – 117° .

W. A. D.

[1-Acetylamino-2:4 diaminonaphthalene.] FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.P. 151768).—1-Acetylamino-2:4-diaminonaphthalene, prepared by reducing 1-acetylamino-2:4-dinitronaphthalene (Meldola, Proc., 1886, 2, 172) with iron and acetic acid, crystallises in slightly brown needles, melts at 189° , and dissolves readily in alcohol or acetic acid, sparingly in benzene. It yields a golden-yellow dye on fusion with sulphur at 160° . C. H. D.

Bases of Triphenylmethane Dyes. ARTHUR HANTZSCH (Ber., 1904, 37, 3434–3440. Compare Abstr., 1900, i, 365).—A reply to Baeyer and Villiger (this vol., i, 786). G. Y.

Nomenclature of the Rosanilines. JULES SCHMIDLIN (Compt. rend., 1904, 139, 504–505).—The author desires to amend the

nomenclature of the rosaniline bases, but considers Baeyer's nomenclature, in which the rosaniline bases are formulated as derivatives of fuchsonimine, too cumbersome. For pararosaniline, he proposes to substitute rosaniline. Rosaniline, magenta, new magenta, aniline-blue, and methyl-violet then become rosamonotoluidine, rosaditoluidine, rosatritoluidine, triphenylrosaniline, and hexamethylrosaniline respectively.

H. M. D.

Tetrahydroxycyclohexanerosanilines—a New Class of Colourless Derivatives. JULES SCHMIDLIN (*Compt. rend.*, 1904, 139, 506—507. Compare this vol., i, 785).—The trihydrochlorides of the rosaniline bases combine with $4H_2O$ in acid solution and form, according to the author, tetrahydroxycyclohexanerosanilines analogous to the tetrachloro- and tetra-amino-cyclohexanerosanilines previously obtained by the absorption of $4HCl$ or $4NH_3$. The hydrochlorides of magenta (rosaditoluidine) and of new magenta (rosatritoluidine) dissolve very readily in concentrated hydrochloric acid, and when kept for 24—48 hours the tetrahydroxy-compounds separate in the form of white crystals. They are stable at the ordinary temperature, but lose four molecules of water at 50° . They are very soluble in water; the concentrated solution slowly deposits magenta in the cold, immediately on warming. The fact that $4HCl$, $4NH_3$, or $4H_2O$ are absorbed leads the author to conclude that the molecule of the rosaniline salts contains four double aliphatic bonds.

H. M. D.

Carbinol Salts and cycloHexanerosanilines; Decolourisation Phenomena. JULES SCHMIDLIN (*Compt. rend.*, 1904, 139, 521—524).—To explain the formation of colourless solutions when the trihydrochlorides of the rosaniline bases are dissolved in excess of mineral acid, it is assumed that four mols. of water are taken up, the quinonoid nucleus being transformed into a cyclohexane ring (compare preceding abstract). This view is supported by thermochemical data. Hexamethylpararosaniline trihydrochloride dissolves in dilute hydrochloric acid giving a coloured solution which, however, soon becomes colourless. During the colour change, 5 cal. are developed. Compared with the total heat change in this case, the heat of solution of the corresponding carbinol trihydrochloride is greater by 5 cal., whilst that of the cyclohexane trihydrochloride is less to the extent of 5 cal. These data do not accord with the view that carbinol salts are present in solution.

It seems probable that, when the rosaniline-carbinols are neutralised by acid, the benzene ring first undergoes transformation into a cyclohexane ring, which by loss of water gives rise to the quinonoid structure.

H. M. D.

Thermochemical Comparison of Rosanilines and Leucanilines. JULES SCHMIDLIN (*Compt. rend.*, 1904, 139, 542—544).—The heats of neutralisation of the rosaniline-carbinols have been measured, and data are given for the formation of (I) the solid monohydrochlorides, (II) the solid trihydrochlorides. The heats of formation of the solid

leucaniline trihydrochlorides from the corresponding solid leuco-bases and aqueous hydrochloric acid are also recorded (III):

| Carbinol bases. | I. | II. | III. |
|------------------------------------|------------|-------------|-------------|
| Pararosaniline (solid) + HCl (aq.) | + 9.9 cal. | + 16.1 cal. | + 12.0 cal. |
| Rosaniline „ „ | 9.6 „ | 16.4 „ | 12.4 „ |
| Magenta C ₂₁ „ „ | 10.9 „ | 16.3 „ | 13.1 „ |
| New magenta „ „ | 11.1 „ | 16.3 „ | 12.8 „ |
| Hexamethyl- pararosaniline „ „ | 13.7 „ | 18.2 „ | 14.3 „ |
| „ „ + HBr (aq.) | 11.4 „ | 15.3 „ | |

It is found that the monohydrochlorides contain H₂O, which is only evolved at about 250°.

The heat development in the formation of the trihydrochlorides is in every case greater for the carbinol salt than for the leuco-salt. In the case of the carbinols, the first molecule of acid develops much more heat than the second or third, and this inequality increases with the strength of the base. The thermal data are in accord with the fact that the bases behave essentially as monoacid bases.

The heats of formation of the tetrahydroxycyclohexane salts from the rosaniline trihydrochlorides are:

| | |
|---|--------------|
| Magenta C ₂₁ trihydrochloride (solid) + 4H ₂ O (liq.) | = + 5.6 cal. |
| New magenta „ „ „ | = 5.5 „ |
| Hexamethyl- pararosaniline „ „ „ | = 7.0 „ |
| | H. M. D. |

Relations between the Safranines, Mauveines, Indulines, Indazines, Naphthyl-red, Naphthyl blue, Rosindulines, and Magdala-red. LUDWIG PAUL (*Chem. Zeit.*, 1904, 28, 777—780).—A theoretical paper unsuitable for abstraction. W. A. D.

[Indophenol Derivatives.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 152689).—Only small quantities of an unstable indophenol are obtained on oxidising a mixture of phenol and *p*-phenylenediamine. By dissolving phenol and 2:6-dichloro-*p*-phenylenediamine in very dilute hydrochloric acid and adding potassium dichromate, a stable *indophenol* is precipitated in the form of a red powder, becoming bronze-like on rubbing; it dissolves in organic solvents to red or violet solutions. A solution of sodium sulphide reduces it to the corresponding diphenylamine derivative, which forms colourless crystals dissolving in sodium hydroxide; the solution becoming oxidised to the indophenol on exposure to air. The *hydrochloride* forms slender, felted needles. C. H. D.

A New Reaction of the Semicarbazones. II. WALTHER BORSCHKE and C. MERKWITZ (*Ber.*, 1904, 37, 3177—3187. Compare Abstr., 1902, i, 186).—The semicarbazones of acetone, acetophenone, benzophenone, β -methylhexanone, *l*-menthone, *d*-camphor, pulegone, and

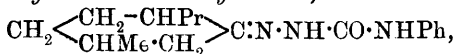
d-carvone react in the normal manner with primary aromatic amines, for instance,

$\text{CMePh:N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2 + \text{NH}_2\text{Ar} = \text{CMePh:N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHAr} + \text{NH}_3$; from the condensation products formed in this manner, the corresponding hydrazides may be obtained by means of dilute hydrochloric acid. The behaviour of the semicarbazones of benzylideneacetone, *o*-hydroxybenzylideneacetone, and methyl-*o*-hydroxybenzylideneacetone, on the other hand, is abnormal.

Benzophenonesemicarbazone, $\text{CPh}_2\text{:N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, prepared from benzophenone and semicarbazide, separates from alcohol in needles, which become liquid at $164\text{--}165^\circ$ and decompose at a higher temperature with the evolution of ammonia and formation of ammonium carbamate, hydrazodicarboxylamide, and benzophenoneazine. When boiled with aniline, it yields *benzophenonephenylcarbamic acid hydrazone*, $\text{CPh}_2\text{:N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$, separating from alcohol in needles and melting at 163° .

3-Methylcyclohexanonephenylcarbamic acid hydrazone, prepared by boiling 3-methylcyclohexanonesemicarbazone with aniline, separates from alcohol in needles and melts at $169\text{--}170^\circ$.

l-Menthonephenylcarbamic acid hydrazone,



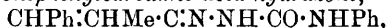
prepared from *l*-menthonesemicarbazone and aniline or by condensation of *l*-menthone with phenylcarbamic acid hydrazide, separates from alcohol in needles and melts at $180\text{--}181^\circ$.

d-Camphorphenylcarbamic acid hydrazone, $\text{C}_{10}\text{H}_{16}\text{:N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$, prepared from *d*-camphorsemicarbazone and aniline, becomes liquid at $153\text{--}154^\circ$. When warmed with dilute hydrochloric acid, it is converted into phenylsemicarbazide hydrochloride and *d*-camphor.

Pulegonephenylcarbamic acid hydrazone forms tiny needles melting at $132\text{--}133^\circ$.

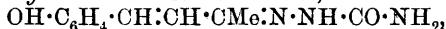
d-Carvonephenylcarbamic acid hydrazone crystallises in needles and melts at $176\text{--}177^\circ$.

Benzylideneacetonephenylcarbamic acid hydrazone,



prepared from benzylideneacetone and semicarbazide, separates from alcohol in yellow leaflets and melts at 187° . When gently boiled with aniline for 8 minutes, it forms *benzylideneacetonephenylsemicarbazone*, which separates from alcohol in tiny needles and melts at 195° . When benzylideneacetonesemicarbazone is further boiled with aniline, diphenylcarbamide and a resin are produced; this resin, when treated with dilute hydrochloric acid and then distilled in steam, yields benzaldehyde, whilst the residue contains benzalazine.

o-Hydroxybenzylideneacetonesemicarbazone,



prepared from *o*-hydroxybenzylideneacetone and semicarbazide hydrochloride, forms yellow needles and melts and decomposes at $206\text{--}207^\circ$. The corresponding *phenylsemicarbazone* separates from alcohol in needles and melts and decomposes at $183\text{--}184^\circ$; the *benzoyl* derivative melts at $204\text{--}205^\circ$. By prolonged boiling with aniline, *o*-hydroxybenzylideneacetonesemicarbazone yields *s*-diphenylcarbamide as the main product,

o-hydroxybenzylideneazine being also formed; the latter melts at 213—214°, and was further identified by conversion into its diacetyl derivative, melting at 190—191°.

2-Hydroxy-5-methylbenzylideneacetone, prepared from 2-hydroxy-5-methylbenzaldehyde and acetone, melts at 128—129°. Its *semicarbazone* melts at 203°, and, when boiled with aniline, forms carbanilide, 2-hydroxy-5-methylbenzylideneacetonephenylsemicarbazone, and 2-hydroxy-5-methylbenzylideneazine. The latter separates from a mixture of chloroform and alcohol in glistening needles and melts at 122°, whilst its *diacetyl* derivative melts at 163°. *2-Hydroxy-5-methylbenzylideneacetonephenylcarbamie acid hydrazone* separates from alcohol in leaflets and melts at 177°.

A. McK.

Semicarbazones of Reducing Sugars. LÉON MAQUENNE and W. GOODWIN (*Bull. Soc. chim.*, 1904, [iii], 31, 1075—1078).—The semicarbazones were prepared by adding a slight excess of semicarbazide, dissolved in alcohol, to a solution of the sugar in water and setting the mixture aside for several days. The melting points recorded were determined on the Maquenne block (*Abstr.*, 1904, ii, 383). The specific rotations quoted are for aqueous solutions.

Arabinosesemicarbazone forms small crystals, melts and decomposes at about 190°, dissolves in 6·5 parts of water at 20°, and has $[\alpha]_D + 25^\circ$ immediately after solution and $+ 23\cdot8^\circ$ after 24 hours (compare Herzfeld, *Zeit. Ver. Rubenzuck. Ind.*, 1897).

Xylosesemicarbazone occurs in brilliant crystals, melts and decomposes at about 202—204°, dissolves in 4·65 parts of water at 21°, and has $[\alpha]_D - 38\cdot8^\circ$ on solution, $- 26\cdot3^\circ$ after 24 hours, and $- 24\cdot4^\circ$ after 48 hours.

Rhamnosesemicarbazone, $C_7H_{15}O_5N_3\cdot\frac{1}{2}H_2O$, was obtained in large crystals melting and decomposing at about 183°. The compound does not become anhydrous at 120°; it dissolves in 22·3 parts of water at 21°, has $[\alpha]_D + 75^\circ$ at the moment of solution, and $+ 50^\circ$ after 120 hours.

Dextrosesemicarbazone, $C_7H_{15}O_6N_3$, melts and decomposes at about 197—198°, dissolves in 50 parts of water at 21° and in 42·5 parts at 25°, and has $[\alpha]_D - 17^\circ$ some minutes after solution and $- 9^\circ$ after 72 hours (compare Breuer, *Abstr.*, 1898, i, 620).

Mannosesemicarbazone, $C_7H_{15}O_6N_3\cdot\frac{1}{2}H_2O$, forms bulky crystals, melts at 117°, or when slowly heated at 108°, dissolves in 14·28 parts of water at 20·5°, and has $[\alpha]_D - 53^\circ$ at first, and $- 43^\circ$ after 24 hours.

Galactosesemicarbazone occurs in small crystals and melts at about 200—202°. The aqueous solution, saturated at 20·5°, contains 8·9 grams per 100 c.c. The substance has $[\alpha]_D + 3\cdot1^\circ$ at first, and $+ 16\cdot9^\circ$ after 48 hours.

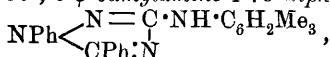
Lactosesemicarbazone, $C_{13}H_{25}O_{11}N_3\cdot 2H_2O$, was obtained in bulky crystals melting and decomposing at about 185°; it loses $1H_2O$ at 115° and a second at 120°, decomposing slightly at the same time. The solution in water, saturated at 20·5°, contains 19·8 grams in 100 c.c. The specific rotation $[\alpha]_D$ is $+ 10\cdot6^\circ$ at first, and $+ 11\cdot25^\circ$ after 24 hours.

Cellosesemicarbazone, $C_{13}H_{25}O_{11}N_3\cdot 2H_2O$, is a crystalline powder

which becomes anhydrous at 115°. Its saturated solution contains 7.2 grams in 100 c.c. at 21°. The substance has $[\alpha]_D - 7.8^\circ$ at first, and -5.2° after 48 hours. T. A. H.

Action of Phenylhydrazine on Benzoyl- ψ -thiocarbamides. 3-Amino-1:5-diphenylpyrro- $\alpha\beta'$ -diazole [3-Amino-1:5-diphenyl-1:2:4-triazole] Derivatives. TREAT B. JOHNSON and GEORGE A. MENGE (*Amer. Chem. J.*, 1904, 32, 358—372. Compare Wheeler and Beardsley, *Abstr.*, 1903, i, 293).—*Methyl benzoyliminothiolcarbonate*, $\text{NBz}\cdot\text{C}(\text{SMe})\cdot\text{OMe}$, obtained by the action of methyl iodide on methyl benzoylthioncarbamate in presence of sodium ethoxide, boils at 200° under 20 mm. pressure, crystallises from light petroleum in colourless prisms, and melts at 43°. Benzoyl-*m*-nitrophenylmethyl- ψ -carbamide (Wheeler and Johnson, *Abstr.*, 1900, i, 635) crystallises from alcohol in acicular prisms and melts at 86—88°.

Benzoyl- ψ -cumylmethyl- ψ -carbamide, $\text{NBz}\cdot\text{C}(\text{OMe})\cdot\text{NH}\cdot\text{C}_6\text{H}_2\text{Me}_3$, prepared from ψ -cumidine and methyl ethyl benzoyliminothiolcarbonate, crystallises from alcohol in needles, melts at 87—89°, and is readily soluble in ether or benzene. When this substance is heated with phenylhydrazine at 130°, 3- ψ -cumylamino-1:5-diphenyltriazole,



is produced, which crystallises from alcohol in rosettes of needles and melts at 121—123°.

By the action of phenylhydrazine on benzoylphenylethyl- ψ -carbamide, 3-anilino-1:5-diphenyltriazole (Wheeler and Beardsley, *loc. cit.*) is produced.

*Benzoyl-*m*-nitrophenylethyl- ψ -carbamide*, $\text{NBz}\cdot\text{C}(\text{OEt})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, prepared from *m*-nitroaniline and ethyl benzoyliminothiolcarbonate, crystallises from alcohol in prisms and melts at 86—88°.

*Benzoyl-*m*-chlorophenylethyl- ψ -carbamide*, $\text{NBz}\cdot\text{C}(\text{OEt})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl}$, from *m*-chloroaniline and ethyl benzoyliminothiolcarbonate, crystallises from alcohol in long, slender prisms and melts at 47—48°; when heated with phenylhydrazine, it is converted into 3-*m*-chlorophenyl-amino-1:5-diphenyltriazole, $\text{NPh} \left\langle \begin{array}{c} \text{N}=\text{C}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl} \\ \text{CPh}\cdot\text{N} \end{array} \right.$, which crystal-

lises from alcohol in short, stout prisms and melts at 195—196°.

*Benzoyl-*p*-tolylethyl- ψ -carbamide*, $\text{NBz}\cdot\text{C}(\text{OEt})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, from *p*-toluidine and ethyl benzoyliminothiolcarbonate, crystallises in needles or prisms, melts at 77—78°, and, when heated with phenylhydrazine, yields 3-*p*-toluidino-1:5-diphenyltriazole (Wheeler and Beardsley, *loc. cit.*).

*Benzoyl-*p*-anisylethyl- ψ -carbamide*, $\text{NBz}\cdot\text{C}(\text{OEt})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, from *p*-anisidine and ethyl benzoyliminothiolcarbonate, crystallises from alcohol in long, slender prisms and melts at 66—67°. By the action of phenylhydrazine on this compound, it is converted into 3-*p*-anisyl-amino-1:5-diphenyltriazole, $\text{NPh} \left\langle \begin{array}{c} \text{N}=\text{C}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe} \\ \text{CPh}\cdot\text{N} \end{array} \right.$, which

crystallises from alcohol in slender prisms and melts at 224—225°.

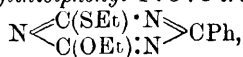
Benzoyl- ψ -cumylethyl- ψ -carbamide, $\text{NBz}\cdot\text{C}(\text{OEt})\cdot\text{NH}\cdot\text{C}_6\text{H}_2\text{Me}_3$, from

ψ -cumidine and ethyl benzoyliminothiolcarbonate, crystallises in prisms and melts at 79—80°.

By the action of phenylhydrazine on benzoyl thiocyanate in ethereal solution, benzoylphenylthiosemicarbazide (m. p. 136°), 3-thiol-1 : 5-diphenyltriazole, and 5-thiol-1 : 3-diphenyltriazole are produced (compare Dixon, Trans., 1889, 55, 304).

When acetonephenylhydrazone is heated with an ethereal solution of benzoyl thiocyanate, the β -propylidene derivative of benzoylphenylthiosemicarbazide, $\text{NHBz}\cdot\text{CS}\cdot\text{NPh}\cdot\text{N}\cdot\text{CMe}_2$, is produced, which crystallises from alcohol in prisms, melts at 136°, and is converted by hydrochloric acid or boiling water into 5-thiol-1 : 3-diphenyltriazole.

By the action of ψ -thiocarbamide on ethyl benzoyliminothiolcarbonate at the ordinary temperature, mercaptan is produced together with *ethoxyethylthiolphenyl-1 : 3 : 5-triazine*,



which crystallises in prisms, melts at 47—48°, and is very stable.

When ethyl benzoyliminothiolcarbonate is treated with an alcoholic solution of hydroxylamine, mercaptan is evolved and 3-ethoxy-5-phenyl-

1 : 2 : 4-oxadiazole, $\begin{array}{c} \text{C}(\text{OEt}) \cdot \text{N} \\ \text{N} = \text{CPh} \end{array} > \text{O}$, is formed, which crystallises from

alcohol in thick prisms, melts at 47—48°, and is freely soluble in benzene, ether, or light petroleum. By the action of ethyl iodide on the silver salt of 5-hydroxy-3-phenyl-1 : 2 : 4-oxadiazole, 5-ethoxy-3-

phenyl-1 : 2 : 4-oxadiazole, $\begin{array}{c} \text{CPh} = \text{N} \\ \text{N} : \text{C}(\text{OEt}) \end{array} > \text{O}$, is produced ; this compound

was first obtained by Falck (Abstr., 1886, 797), who regarded it as a compound in which the ethyl group is attached to nitrogen.

Benzoyl isocyanochloride, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{N}\cdot\text{CCl}_2$, obtained by the action of chlorine on a solution of benzoyl thiocyanate in chloroform, is an oily liquid which boils at 146—148° under 31 mm. pressure, reacts readily with water, alcohols, or amines, has a very penetrating odour, and attacks the eyes.

E. G.

Preparation of 8-Xanthinecarboxylic Acids. C. F. BOEHRINGER & SÖHNE (D.R.-P. 153121).—The 8-trichloromethylxanthines (this vol., i, 340) are hydrolysed to carboxylic acids, which readily lose carbon dioxide, so that the corresponding xanthines are generally obtained directly (this vol., i, 686). The reaction may be arrested at the first stage by boiling the chloro-compound with water for a short time, or by warming with sodium acetate, or by heating with alcohol and hydrolysing the resulting ester.

3-Methyl-8-trichloromethylxanthine crystallises from glacial acetic acid in prisms and decomposes above 300°. Boiling water converts it into 3-methylxanthine-8-carboxylic acid, crystallising from water in glistening leaflets containing $2\text{H}_2\text{O}$; the ethyl ester melts at 304—305° and the methyl ester at 290—291°.

8-Trichloromethylcaffeine yields caffeinecarboxylic acid (Gomberg, Abstr., 1895, i, 628).

Ethyl theobrominecarboxylate, from 8-trichloromethyltheobromine and

alcohol, forms felted needles and melts at 300° , the *methyl* ester melts at 270° . Potassium hydroxide forms *theobrominecarboxylic acid*, crystallising in short needles and melting at 345° . The *potassium* salt forms slender needles.

C. H. D.

Preparation of 7':8-Dichlorocaffeine. C. F. BOEHRINGER & SÖHNE (D.R.-P. 153122).—7':8-Dichlorocaffeine (this vol., i, 188) may be prepared by the action of dry chlorine on caffeine or 8-chlorocaffeine at 100 — 110° .

C. H. D.

Oxidation of Uric Acid in Alkaline Solution. ROBERT BEHREND (*Annalen*, 1904, 333, 141—160. Compare following abstract).—Since Fischer (Abstr., 1899, i, 392; 1900, i, 63) has shown that both 1- and 7-methyluric acids yield the same β -methylallantoin, and 3- and 9-methyluric acids the same α -methylallantoin, it has become obvious that in the oxidation of uric acid in an alkaline medium to allantoin, one of the five-membered rings is not simply broken, but that a more complicated process takes place, both rings being probably broken and one again regenerated.

Many experiments have been made with the object of throwing further light on the chemical changes involved in the oxidation of uric acid in alkaline solution. In the first place, the temperature and the amount of alkali were varied, the proportion of permanganate being kept constant, one atom of oxygen to 1 mol. of uric acid.

That allantoin is not the first product of the oxidation is shown by the fact that a solution of allantoin in cold dilute alkali hydroxide is completely decomposed in two days, whereas if the product of oxidation of uric acid, which is strongly alkaline, is kept for eight weeks, allantoin can still be readily isolated. All the allantoin is only destroyed after six days at a temperature of 35 — 40° ; the strongly alkaline product of the oxidation can even be evaporated to dryness on the water-bath without all the allantoin being destroyed.

Another substance, uroxanic acid, is always formed together with allantoin when uric acid is oxidised by permanganate or oxygen in alkaline solution. The amount of alloxantoin varies only slightly with the concentration of the alkali and with the temperature, but the amount of uroxanic acid is largely dependent on the concentration of the alkali. When 3 mols. of potassium hydroxide are used for each mol. of uric acid, no uroxanic acid is formed; with increasing excess of the alkali, up to 5 or 6 mols., of the hydroxide to 1 mol. of uric acid, the yield of the acid increases to 23—24 per cent. of the theoretical; a further increase of the alkali is without influence. The amount of alkali is, however, without influence on the course of the oxidation, for it is immaterial to the yield of uroxanic acid whether the excess of alkali is added during the oxidation or only before the subsequent evaporation. One substance is formed by the oxidation, which is then converted into uroxanic acid by heating with the excess of alkali.

The uroxanic acid cannot be regarded as the original oxidation product of the uric acid, since it can be heated for many hours in the solution without undergoing any marked decomposition.

All the evidence then points to the view that a single substance is

formed on the oxidation of uric acid in alkaline solution, which on acidification with acetic acid is converted into allantoin, and on heating with excess of alkali hydroxide into uroxic acid, but if evaporated in the absence of excess of alkali, is changed into other still unknown products. In certain experiments, it is shown that the sum of the allantoin and the uroxic acid represent all the uric acid employed.

Although the constitution of uroxic acid is not finally settled, it is very probably the diureide of malonic acid, $(\text{NH}_2 \cdot \text{CO} \cdot \text{NH})_2 \text{C}(\text{CO}_2\text{H})_2$. There is evidence (which will be published in a future communication) that the first product of oxidation of uric acid is hydroxyglycoluril-carboxylic acid, $\text{CO} < \begin{array}{c} \text{NH} \cdot \text{C}(\text{CO}_2\text{H}) \cdot \text{NH} \\ \text{NH} \cdot \text{C}(\text{OH}) \cdot \text{NH} \end{array} > \text{CO}$; this is next converted into the compound $\begin{array}{c} \text{NH} \cdot \text{CH}(\text{OH}) \\ \text{CO} \text{---} \text{NH} \end{array} > \text{C}(\text{OH}) \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, which then on acidification yields carbon dioxide and allantoin, or, on evaporation with alkali, takes up the elements of water with the production of uroxic acid.

K. J. P. O.

Constitution of β -Methylallantoin. LUDWIG SIMONSEN (*Annalen*, 1904, 333, 101—141).—Since the constitution of both the α - and β -methylallantoins, which are obtained from 1- and 7-methyluric acids and from 3- and 9-methyluric acids respectively, is still in doubt, an attempt has been made to ascertain that of the β -compound by synthesis from methylhydantoin and carbamide.

To prepare hydantoin, the decomposition of glycoluril is recommended; the substance last mentioned is obtained by treating glyoxal (prepared by oxidising paraldehyde with nitric acid) with carbamide in the presence of hydrochloric acid; the glycoluril is best hydrolysed by boiling with concentrated hydrochloric acid, evaporating to a small bulk, and then adding alcohol, when the hydantoin crystallises out, a yield of 75 per cent. being obtained. Methylhydantoin was easily prepared in the usual manner, but dimethylhydantoin could not be obtained.

Attempts to prepare bromo-derivatives of hydantoin failed; the action of bromine is very slow in the absence of a carrier, such as iron wire; when $\frac{1}{2}$ mol. of bromine is used for each mol. of hydantoin, isallituric acid, $\text{CO} < \begin{array}{c} \text{NH} \cdot \text{CH} \cdot \text{N} \text{---} \text{CH}_2 \\ \text{NH} \cdot \text{CO} \quad \text{CO} \cdot \text{NH} \end{array} > \text{CO}$, an oxidation product of hydantoin, is obtained in a yield of 84 per cent.; it crystallises in sparingly soluble prisms, which become coloured at 250° and melt and decompose at $258\text{--}260^\circ$. It can be boiled with concentrated nitric acid and is only attacked by boiling permanganate; ammonia is slowly evolved when it is boiled with concentrated potassium hydroxide. It dissolves readily in ammonia, the solution with silver nitrate giving a silver salt, $\text{C}_6\text{H}_4\text{O}_4\text{N}_4\text{Ag}_2$. This acid appears to be isomeric with Schlieper's allituric acid (*Annalen*, 1845, 56, 20).

When larger proportions of bromine are used, parabanic acid is formed, the dibromo-derivative, $\text{CO} < \begin{array}{c} \text{NH} \cdot \text{CBr}_2 \\ \text{NH} \cdot \text{CO} \end{array} >$, being probably first produced.

Methylhydantoin is converted by bromine under all conditions into *aa*-dimethylisoallituric acid, $\text{CO} \begin{array}{c} \text{NH}-\text{CH}\cdot\text{N}-\text{CH}_2 \\ \text{NMe}\cdot\text{CO} \quad \text{CO}\cdot\text{NMe} \end{array} \text{CO}$, which crystallises in leaflets, fairly soluble in hot water and melting at $208-210^\circ$; it remains unchanged when heated with concentrated nitric acid.

β -Nitroisoallituric acid, $\text{C}_6\text{H}_5\text{O}_4\text{N}_4\cdot\text{NO}_2$, cannot be prepared by boiling isoallituric acid with nitric acid, but only by treatment with a mixture of nitric acid and phosphoric oxide at $50-60^\circ$; it forms a micro-crystalline powder melting and decomposing between 170° and 195° and is decomposed by heating with water, oxalic acid and hydantoin being produced. It dissolves in sodium hydroxide with a yellow coloration, acids precipitating oxaluric acid and hydantoin from the solution.

β -Nitro-*aa*-dimethylisoallituric acid, prepared in the same manner as the nitro-compound last mentioned, crystallises in prisms melting and decomposing between 170° and 190° , and is decomposed when boiled with water into α -methylhydantoin, oxalic acid, nitric oxide, and carbon dioxide. It dissolves in alkali hydroxides with a yellow coloration and is thereby decomposed into methyloxaluric acid (which, on acidification, separates in prisms and melts and decomposes at $177-178^\circ$), α -methylhydantoin (m. p. $181-182^\circ$), oxalic acid, and nitrous acid.

β -Acetyl-*aa*-dimethylisoallituric acid, $\text{C}_6\text{H}_3\text{O}_4\text{N}_4\text{Me}_2\text{Ac}$, prepared by boiling dimethylisoallituric acid with acetic anhydride, crystallises in leaflets melting at $193-194^\circ$.

Attempts to hydrolyse isoallituric acid with concentrated hydrochloric acid led to the production of an amino-acid yielding a blue copper salt, but it could not be obtained pure.

$\alpha\beta$ -Diacetylhydantoin, $\text{CO} \begin{array}{c} \text{NAc}\cdot\text{CH}_2 \\ \text{NAc}\cdot\text{CO} \end{array}$, is formed when hydantoin is boiled with acetic anhydride, and crystallises in leaflets melting at $104-105^\circ$; when boiled with water, it is converted into β -acetylhydantoin (m. p. $143-144^\circ$). β -Acetyl- α -methylhydantoin, prepared from α -methylhydantoin, crystallises in long needles melting at $134-135^\circ$.

When $\alpha\beta$ -diacetylhydantoin is boiled with a solution of bromine in acetic acid, acetylhydantoin is alone formed; β -acetyl- α -methylhydantoin, on the other hand, is largely converted into *aa*-dimethylisoallituric acid (m. p. $208-210^\circ$), a fact which indicates that the two nuclei are linked together by the nitrogen atoms (compare above).

As the result of a long series of experiments, it was found that allantoin is best prepared from hydantoin and carbamide by boiling a solution of hydantoin (4 grams), bromine (6.4 grams), and carbamide (0.2 gram) in 25 c.c. of acetic acid, and after 10 minutes adding 3 grams of carbamide dissolved in 20 c.c. of acetic acid; the product is evaporated and the hydantoin extracted with alcohol. In a similar manner, β -methylallantoin was prepared from α -methylhydantoin and proved to be identical with the substance obtained by Fischer from 1- or 7-methyluric acid.

This synthesis shows that β -methylallantoin is represented by the formula $\begin{array}{c} \text{CO}-\text{NH} \\ \text{NMe}\cdot\text{CO} \end{array} \text{CH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$.

K. J. P. O.

Certain Nitrogen Compounds. FREDERICK J. ALWAY and REUBEN M. PINCKNEY (*Amer. Chem. J.*, 1904, 32, 398—400).—*m*-Nitrobenzene-*p*-azobenzaldehyde, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$, obtained by the condensation of *p*-nitrobenzaldehyde with *m*-nitroaniline in presence of acetic acid, forms orange-red, indistinctly crystalline masses, melts at 223° , and is sparingly soluble in alcohol or acetic acid.

Ethyl p-nitrosobenzoate, obtained by reducing ethyl *p*-nitrobenzoate with zinc dust and acetic acid and treating the product with chromic acid, crystallises in yellow needles, melts at 81° , and forms green solutions; ethyl *p*-azoxybenzoate (Meyer and Dahlem, *Abstr.*, 1903, i, 448) is also produced in this reaction. E. G.

***o*-Hydroxyazo-Dye from 2:4-Dichloro-*a*-naphthylaminesulphonic Acid.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 153298).—2:4-Dichloro-*a*-naphthylaminesulphonic acid, prepared by the action of fuming sulphuric acid on 2:4-dichloroacetyl-*a*-naphthalide, is a colourless powder, dissolving sparingly in water. The sodium, zinc, and magnesium salts form colourless crystals. The diazonium compound forms yellow dyes with resorcinol, &c., in alkaline solutions, but when solutions containing alkali acetates or carbonates are employed, deep violet dyes are obtained. In this case, the chlorine atom in the ortho-(β)-position is replaced by hydroxyl. The same result is obtained when the amino-acid is treated with sodium nitrite without the addition of mineral acid. The violet dyes from resorcinol or β -naphthol yield fast blue-black shades on subsequent treatment with chromium salts. C. H. D.

Diazo-compounds [an Explanation]. ARTHUR HANTZSCH (*Ber.*, 1904, 37, 3030).—The author's criticisms (this vol., i, 201) referred to Euler's theoretical conclusions, and not to his experimental results.

G. Y.

Diazotisation of Sulphonated *m*-Diamines. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 152879).—It has not been possible hitherto to diazotise one amino-group in sulphonated *m*-diamines. It may, however, be performed by mixing the diamine with the calculated quantity of alkali nitrite and then adding the mineral acid, or otherwise, so that the diamine is always in presence of the requisite quantity (1 mol.) of free nitrous acid. The diazotisation of several diaminosulphonic acids is described in detail. C. H. D.

Electrolytic Preparation of Azo-dyes. C. F. BOEHRINGER & SÖHNE (D.R.-P. 152926).—Azo-dyes may be prepared by electrolysing a solution of sodium nitrite containing an aromatic amine in solution or suspension, together with an acid substance capable of combining with the diazonium compound formed. The NO_2 ions travel towards the anode. The anode cell contains the solution or suspension, which may be neutral or alkaline, with a platinum anode. The cathode may be of any convenient metal, and is immersed in dilute sodium hydroxide, being separated from the anode cell by a diaphragm. The strength of current may vary within wide limits. Cooling is not necessary, as

the formation of the azo-compound proceeds faster than the decomposition of the diazonium salt, and the reaction is even facilitated by warming. C. H. D.

The Fluorazones, a New Group of Dyes produced from Aminoazo-dyes by Fusion with Resorcinol. LUDWIG PAUL (*Chem. Zeit.*, 1904, 28, 765—772).—The *fluorazones* are fluorescent dyes, obtained by heating aminoazo-compounds with resorcinol. *Fluorazone S* is obtained by heating benzeneazo-*a*-naphthylamine or *p*-sulphobenzeneazo-*a*-naphthylamine with resorcinol; it is insoluble in water, but dissolves in alcohol, imparting to it a violet colour; it is dichroic and shows a red fluorescence. *Fluorazone L*, which is formed with fluorazone S when *p*-sulphobenzeneazo-*a*-naphthylamine is heated with resorcinol, is soluble in water. Several fluorazones, for example, those obtained from Meldola's base (*p*-aminobenzeneazo-*a*-naphthylamine), from *p*-hydroxybenzeneazo-*a*-naphthylamine, and from aminoazonaphthalene, are described, but their chemical nature has not been investigated; no analyses are recorded. W. A. D.

Preparation of Polyazo-Dyes from 8-Amino-*a*-naphthol-3:6-disulphonic Acid. SCHOELLKOPF, HARTFORD & HANNA Co. (D.R.-P. 153557).—Polyazo-dyes are obtained by combining 1 mol. of a tetrazonium compound in acid solution with 1 mol. of 8-amino-*a*-naphthol-3:6-disulphonic acid. The intermediate compound thus formed is combined in alkaline or sodium acetate solution with a diazonium compound and a phenol or amine. The dyes have the constitution

$$\text{R}^1\text{N}_2\cdot\text{R}\cdot\text{N}_2\cdot\underset{\text{SO}_3\text{Na}}{\underset{|}{\text{C}}}\cdot\underset{\text{C}(\text{OH})\cdot\text{C}\cdot\text{N}_2\text{R}^1}{\underset{|}{\text{C}}}(\text{NH}_2)\cdot\underset{\text{CH}}{\underset{|}{\text{C}}}\cdot\text{CH}=\text{C}\cdot\text{SO}_3\text{Na}.$$

C. H. D.

Albumins Soluble in Acetic Acid and Bence-Jones' Albumosuria. GUSTAVE PATEIN (*J. Pharm. Chim.*, 1904, [vi], 20, 49—55. Compare Abstr., 1904, ii, 599).—It is regarded as probable, from experiments with the proteids of egg-white and serum, that between the albumins and the albumoses there exists an intermediate stage in which coagulation by heat is not easily obtained, and under the influence of weak acids, such as acetic, may be altogether absent. In two cases of Bence-Jones' albumosuria the proteid found was not a true albumose but a globulin. W. D. H.

Hydrolysis of Casein. ZDENKO H. SKRAUP (*Monatsh.*, 1904, 25, 633—656. Compare this vol., i, 538).—A detailed account of the author's method of isolating the crystalline products of the hydrolysis of casein is now given.

In addition to the products mentioned previously (*loc. cit.*), aspartic acid has been obtained.

Diaminoglutaric acid forms a *hydrochloride*, which crystallises in sheaves of needles, and a *platinichloride* and an *aurichloride* which crystallise in long, irregular needles. Aminohydroxysuccinic acid crystallises in white plates; the *copper* salt crystallises in long, blue aggregates of prisms, containing 4H₂O, and is soluble in water.

d-Caseic acid has $[\alpha]_D + 0.13^\circ$; the hydrochloride crystallises in plates; the yellow *platinichloride* forms a crystalline mass; the *aurichloride* crystallises in flower-like aggregates. The inactive caseic acid forms salts identical with those from the dextrorotatory modification.

Diaminoglutaric, diaminoadipic, caseanic, and caseic acids give a yellow coloration with α -naphthol and concentrated sulphuric acid.

G. Y.

Protokyrines. MAX SIEGFRIED (*Chem. Centr.*, 1904, ii, 908; from *Ber. k. sächs. Ges. Wiss. Math. phys. Cl.*, 1904, 117—122. Compare Abstr., 1903, i, 586).—*Caseinokyrine*, prepared in a similar manner to glutokyrine, by decomposition of casein with hydrochloric acid and isolation as the sulphate, has a strong alkaline reaction and absorbs carbon dioxide from the air. The composition of the sulphate is not affected by repeated crystallisation, and the quantity of nitrogen contained in the decomposition products of each crystalline fraction was found to be the same. The sulphate has a strongly acid reaction and is readily soluble in water, but insoluble in absolute alcohol or ether. Caseinokyrine gives the biuret reaction, but the coloration is not as red as that shown by peptones which have been formed by the action of enzymes. *Caseinokyrine phosphotungstate* crystallises in groups of needle-shaped prisms. The formula of the sulphate, $C_{23}H_{47}N_9O_8 \cdot 3H_2SO_4$ [?], is derived from the results of analysis on the assumption that a small quantity of alcohol used in the preparation of the salt is obstinately retained. Arginine and lysine have been isolated from the decomposition products of caseinokyrine, but neither ammonia nor histidine could be detected. By the action of sulphuric acid, glutamic acid is also formed. The bases which are obtained when caseinokyrine is completely hydrolysed contain more than 80 per cent. of the nitrogen of the original kyrine.

Since histidine is formed by the complete hydrolysis of casein, but not of caseinokyrine, the histidine complex is either not present in the casein molecule (if such exists), or only in a state of feeble combination. Fibrin also yields a kyrine; the composition of the sulphate is very similar to that of caseinokyrine.

E. W. W.

Oxidation of Proteids with Calcium Permanganate. I. Oxidation of Gelatin. FRIEDRICH KUTSCHER and MARTIN SCHENCK (*Ber.*, 1904, 37, 2928—2931. Compare Kutscher and Zickgraf, Abstr., 1903, i, 666).—The product obtained on oxidising a boiling solution of gelatin in water by means of calcium permanganate, after addition of ammonium carbonate and filtration, deposits white needles, apparently of oxaluramide. The filtrate deposits long needles of ammonium oxamate on evaporation. The immediate source of the ammonium oxamate must be glycine, which yields oxamic acid on oxidation with permanganates.

C. H. D.

Hydrolysis of Spleen Nucleic Acid by Dilute Mineral Acid. PHOEBUS A. LEVENE (*Amer. J. Physiol.*, 1904, 12, 213—219).—When spleen nucleic acid is hydrolysed by 2 per cent. sulphuric acid at 100—125°, the main substances in solution are purine bases. The

residue resembles Neumann's nucleo-thyminic acid, and on further decomposition yields purine and pyrimidine bases; the yield of purine bases is small, and the amount of pyrimidine bases is also reduced in quantity as compared with that in the original nucleic acid. The substance which yields furfuraldehyde is almost wholly broken up by treatment with 2 per cent. sulphuric acid, and so is in loose combination in the original molecule. On the other hand, the yield of lævulic acid is so large after this treatment that a hexose or very stable polysaccharide must be in firm combination. W. D. H.

The Combination of Purine Bases in the Nucleic Acid Molecule. RICHARD BURIAN (*Zeit. physiol. Chem.*, 1904, 42, 297—298. Compare this vol., i, 358).—Polemical against Steudel. W. D. H.

Chemical Composition of Adrenaline (Epinephrine). GABRIEL BERTRAND (*Compt. rend.*, 1904, 139, 502—504. Compare this vol., i, 791, i, 540).—One hundred and twenty-five grams of crystallised adrenaline were obtained by working up the glands from about 4000 horses. One hundred and ten grams of this material were dissolved in acid and divided into seven fractions by successive addition of ammonia to the solution. Each of these fractions was further subjected to similar treatment. The analyses of the products obtained at different stages are very concordant and indicate the purity of the original adrenaline, the composition of which is represented by $C_9H_{13}O_3N$. For the molecular weight in acetic acid, 174.3 was obtained (theory 183) (compare Jowett, *Trans.*, 1904, 85, 192). H. M. D.

Studies on Enzyme Action II. Rate of the Change conditioned by Sucroclastic Enzymes, and its Bearing on the Law of Mass Action. E. FRANKLAND ARMSTRONG (*Proc. Roy. Soc.*, 1904, 73, 500—516. Compare *Trans.*, 1903, 83, 1305).—The author has studied the action of lactase and emulsin on milk sugar, and of maltase on maltose, and the results obtained, taken in conjunction with those of earlier workers (Adrian Brown, *Trans.*, 1902, 81, 373; Horace Brown and Glendinning, *ibid.*, 388), strongly support the view that the rate of change is essentially dependent on the relative proportions of enzyme and sugar. On the hypothesis that the enzyme combines with the sugar, the effects of varying the conditions may be predicted as follows in harmony with the observed facts: (1) if the amount of enzyme is small, relatively to the initial amount of sugar, the change is at first a linear function of the time; as hydrolysis proceeds, and the amount of enzyme is relatively greater, the change is approximately a logarithmic function of the time, as required by the law of mass action. (2) If the amount of enzyme is initially considerable compared with the amount of sugar, the linear part of the change is not apparent. (3) When the amount of enzyme decreases during hydrolysis, owing to the influence of the products, the rate of change will be governed by an equation of the second order, so that the values of the velocity constant K , calculated for the simple logarithmic formula, will gradually diminish. (4) If the amounts of enzyme and

water are kept constant, an increase in the amount of sugar beyond that required for complete combination with the enzyme will not augment the quantity of hydrolyte undergoing change in a given time. The proportion of the hydrolyte changed, and the value of K , will, however, decrease as the sugar concentration is increased.

J. C. P.

Studies on Enzyme Action. III. Influence of the Products of Change on the Rate of Change conditioned by Sucroclastic Enzymes. E. FRANKLAND ARMSTRONG (*Proc. Roy. Soc.*, 1904, 73, 516—526. Compare preceding abstract).—In the previous paper, retardation of the hydrolysis of a sugar was attributed to the influence of the products of change on the enzyme. The extent of this influence has been studied, and it is found that in the hydrolysis of lactose by lactase, retardation is due to galactose, whilst dextrose and lævulose are almost without influence. The hydrolysis of lactose by emulsin is considerably retarded by dextrose, slightly by galactose, and not perceptibly by lævulose. The relative effect of dextrose, galactose, and lævulose on the hydrolysis of maltose by maltase is the same as that just mentioned. Hydrolysis by invertase, on the other hand, is retarded by lævulose, but not by dextrose. When Fischer's observations are taken into account, it is seen that the only hexoses which retard hydrolysis by any given enzyme are those derived from the hexosides which that enzyme can hydrolyse. This result is proof of the closely-related configurations of enzyme and hydrolyte, and may be taken as evidence that the enzyme combines with the hexose in such a way that it is withdrawn from the sphere of action.

It is noteworthy that the action of emulsin on lactose is retarded not only by dextrose, but also, although to a less extent, by α -methylglucoside, which is not itself attacked by emulsin. So also α -methylgalactoside, although unaffected by the enzyme, retards the hydrolysis of lactose by lactase just as much as galactose itself. On the other hand, α -methylglucoside, like dextrose, has no retarding influence on the hydrolysis of lactose by lactase. Further, the action of maltase on maltose is retarded by β -methylglucoside, which is unaffected by that enzyme. Consideration of these and other facts leads to the view that enzyme and hydrolyte must be in complete correlation, and are probably attached along the line of carbon atoms.

J. C. P.

Studies on Enzyme Action. IV. Sucroclastic Action of Acids as contrasted with that of Enzymes. E. FRANKLAND ARMSTRONG and ROBERT JOHN CALDWELL (*Proc. Roy. Soc.*, 1904, 73, 526—537. Compare preceding abstracts).—The results of the experiments described in this paper are summarised as follows. The hydrolysis of lactose in presence of hydrochloric acid takes place in accordance with the logarithmic law, although in concentrated solutions there is a marked tendency for reversion to take place, with the result that the course of change in its later stages departs from the said law. The rate of hydrolysis for lactose is remarkably slow compared with that for sucrose, but the effect of increasing the concentration resembles that produced by changes of concentration in the case of sucrose and

maltose. The products of hydrolysis exert an influence on the rate of change comparable with that exercised by lactose itself. Rise of temperature has even more influence on the rate of hydrolysis of lactose than on that of sucrose.

So far as the theory of hydrolysis by acids is concerned, the authors take a view similar to that adopted in the case of enzyme action. It is supposed that an active system is formed by a combination of a part of the sugar with a part of the acid, and that at a given temperature there will be an equilibrium between water, sugar, and acid. This view of hydrolysis as depending on association affords an explanation of the great influence of temperature-changes on the rate of hydrolysis. Emphasis is laid also on the differences in the behaviour of enzymes and acids as hydrolytic agents. The two important points in this connection are (1) the superior affinity of the enzymes for the carbohydrates; (2) the very different behaviour of enzymes and acids towards water—a consequence of the colloid nature of the former and the crystalloid nature of the latter.

J. C. P.

Enzyme Action as bearing on the Validity of the Ionic Dissociation Hypothesis and on the Phenomena of Vital Change. HENRY E. ARMSTRONG (*Proc. Roy. Soc.*, 1904, 73, 537—542).—The selective character of the influence exerted by enzymes (see previous abstracts) is regarded as final proof that the action depends not on dissociation, but on association. This view is held also with regard to the hydrolysis of sugars by acids and chemical change generally.

The conception of the enzyme as associated at several points with the carbohydrate molecule is discussed in relation to fermentative changes, and it is further thought probable that this conception will furnish an interpretation of many hitherto unexplained phenomena.

J. C. P.

Lability of Enzymes. KEIJIRŌ ASŌ (*Bul. Coll. Agric. Tōkyō*, 1904, 6, 57—75).—Small amounts of dicyanogen do not destroy enzymes in a very diluted condition. Nitrous acid is more injurious than equally diluted nitric acid.

Enzymes are destroyed by dilute neutral solutions of hydrazine, methylhydrazine, and hydroxylamine. This would accord with the assumption that the active grouping in the enzymes is ketonic (Loew) or aldehydic.

N. H. J. M.

Action of Hydrogen Peroxide on Enzymes. ALB. J. J. VANDEVELDE (*Beitr. chem. Physiol. Path.*, 1904, 5, 558—570).—Hydrogen peroxide favours the action of rennin, pepsin, trypsin, and the proteolytic enzyme of milk. It has no such action on katalase or on diastatic ferments; these it inhibits. This difference is explicable on Loew's "lability hypothesis."

W. D. H.

Invertase from Yeast. B. HAFNER (*Zeit. physiol. Chem.*, 1904, 42, 1—34).—Invertase has been obtained by Osborne's method

(Abstr., 1899, i, 967) from a pure press yeast and also from a "bottom" beer yeast. The amount of invertase in the former case was small; it contains, however, only a small amount of ash (2—4 per cent.), and different specimens vary but little in composition. The yield from the "bottom" yeast is much better, but the product is not so pure. It has been found that the invertase from press yeast is far more sensitive to the action of alcohol or ammonia than that obtained from bottom yeast.

It has not been found possible to remove the phosphoric acid entirely from yeast either by precipitation as magnesium ammonium phosphate or by prolonged dialysis. The conclusion is drawn that a considerable amount of the phosphoric acid is in a state of combination in the diastase molecule. This is confirmed by an examination of the ash, which contains a much larger amount of phosphoric acid than could be combined with the bases present in the ash.

It has also not been found possible to obtain an active diastase preparation free from carbohydrate. When the preparation is subjected to prolonged dialysis, considerable amounts of the active ferment and of the carbohydrate pass through the membrane, and the solution left in the inner vessel is not free from carbohydrate. It is thought probable that part, at any rate, of such carbohydrate forms an integral part of the diastase molecule.

The nitrogen contained in the diastase molecule does not form part of a complex nitrogenous group such as albumose, peptone, &c., since (1) preparations of the ferment do not lose their activity when subjected to prolonged treatment with trypsin solution and (2) diastase does not give the biuret reaction.

An apparatus is described for keeping the inner and outer liquids in motion during dialysis.
J. J. S.

Yeast Catalase. WLADIMIR ISSAEW (*Zeit. physiol. Chem.*, 1904, 42, 102—116. Compare Loew, Abstr., 1901, i, 435; 1903, i, 544; Senter, *ibid.*, 1903, ii, 661, and Neumann-Wender, this vol., i, 542).—The greater part of yeast catalase is precipitated when yeast extracts are mixed with their own weight of alcohol, and the activity is not increased by redissolving and precipitating a second time. The activity of the solutions appears to reach its maximum at 40°; it is less at 0° and at 50° and is completely destroyed by boiling for 15 minutes. The decomposition of hydrogen peroxide by the catalase is a true enzymatic reaction and at any time is proportional to the concentration of the peroxide provided the concentration is not too great. In this case, probably, secondary reactions such as the oxidation of the catalase occur. The amount of decomposition is not directly proportional to the amount of enzyme, and when the amount of enzyme is considerable the reaction appears to be no longer unimolecular. When subjected to dialysis, the enzyme becomes less active. The presence of small amounts of potassium dihydrogen phosphate appears to favour the decomposition, but even small amounts of sulphuric acid have an unfavourable effect.
J. J. S.

Yeast Oxydase. WLADIMIR ISSAEW (*Zeit. physiol. Chem.*, 1904, 42, 132—140. Compare Grüss, Abstr., 1901, ii, 615).—An oxydase has

been extracted from yeast by the aid of water or glycerol, and its action at constant temperature on various substances studied. It can not merely oxidise the reducing substances present in the yeast extract, but, if these are previously oxidised by passing air through the solution, it will then oxidise other substances, such as quinol, pyrogallol, &c. The amount of oxydase is often small, and on this account it is sometimes difficult to obtain good oxidation phenomena. Top yeasts appear to contain more than bottom yeasts. J. J. S.

The Activity of Zymase and of Endotryptase in Dead Yeast Cells under Varying Conditions. T. GROMOFF and O. GRIGORIEFF (*Zeit. physiol. Chem.*, 1904, 42, 299—329).—Commercial zymine contains a strong proteolytic enzyme (E. Buchner's endotryptase), the activity of which is largely destroyed by the presence of sucrose, dextrose, lactose, mannitol, alcohol, quinine, glycine, or glycerol. In the case of sucrose, the retardation appears to be proportional to the concentration.

When isotonic solutions of different substances are employed, the retardations are very different, being greatest with sucrose and least with glycine. This can be explained by supposing that with certain reagents, for example, sucrose, proteid synthesis as well as proteolysis occurs. The products of decomposition also appear to retard proteolysis. Certain mineral salts such as calcium chloride or potassium nitrate in dilute solutions accelerate the decomposition either alone or in the presence of sucrose or dextrose.

Experiments have been conducted on the activity of zymase contained in commercial zymine mainly in the form of roll (cylinder) cultures. The amount of carbon dioxide evolved depends largely on the nature of the culture medium; if this contains fermentable substances, the amount of carbon dioxide evolved per hour is greater than when only non-fermentable substances (mannitol or lactose) are present. In the latter case, the amount of carbon dioxide evolved is exactly the same as in self-fermentation. The amount of carbon dioxide evolved per hour gradually decreases, and finally becomes nil owing to the destruction of the zymase by the endotryptase. The addition of fresh zymine again induces evolution of carbon dioxide, but in increased quantity, indicating that the products of fermentation accelerate the decomposition; this is confirmed by the fact that the amounts of carbon dioxide evolved by 1 and 2 grams respectively of zymine are in the ratio 1 : 3.

No differences can be detected when the experiments are conducted in oxygen or in hydrogen. The concentration of the sucrose does not affect the amount of carbon dioxide, but poisonous substances (alcohol, quinine) and salt solutions (calcium chloride and potassium nitrate) have exactly opposite effects to those described in the case of the proteolytic enzyme. J. J. S.

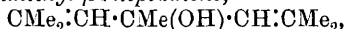
Organic Chemistry.

Oxidation of Methyl and Ethyl Alcohols at their Boiling Points RENÉ DUCHEMIN and JACQUES DOURLÉN (*Compt. rend.*, 1904, 139 679—681).—The authors find that when methyl or ethyl alcohol is distilled in a reflux apparatus, either alone or in the presence of copper, lead, tin, or zinc shot, it is oxidised to formic or acetic acid respectively, the quantity of the acid increasing with the duration of the distillation and varying with the nature of the metal employed, being greatest in the case of copper. In the experiments described, the free acid was titrated with *N*/100 sodium hydroxide in the presence of phenolphthalein, correction being made for the initial acidity of the alcohol employed. The formation of acetic acid from alcohol in these circumstances is probably due to the dehydrogenation of the alcohol in the presence of the metal to form the metallic hydride and aldehyde; the former is broken down into its elements as the reaction proceeds, and the latter is oxidised to acetic acid by the oxygen dissolved in the alcohol. The oxidation of alcohol in the presence of metals has already been investigated by Sabatier and Senderens (compare Abstr., 1903, i, 393, 453) and by Trillat (compare Abstr., 1903, i, 222; ii, 589). M. A. W.

Action of Magnesium Methyl Iodide on Mesityl Oxide and Phorone. TH. VON FELLEBERG (*Ber.*, 1904, 37, 3578—3581).—Magnesium alkyl haloids react with $\alpha\beta$ -unsaturated ketones, yielding doubly unsaturated hydrocarbons, the tertiary alcohols at first formed being unstable (Grignard, Abstr., 1900, i, 382). In the case of mesityl oxide and phorone, it is possible to isolate the alcohols.

β -Hydroxy- $\beta\delta$ -dimethyl- γ -pentene, $\text{CMe}_2\cdot\text{CH}\cdot\text{CMe}_2\cdot\text{OH}$, prepared from mesityl oxide and magnesium methyl iodide, forms a colourless, aromatic liquid, boiling at 46° under 14 mm. pressure and having a sp. gr. 0.8397 at $22.5^\circ/4^\circ$, $\mu = 1.44009$ at 22.5° , and a molecular refraction 35.815. When distilled under the ordinary pressure or with sodium, water is removed and $\beta\delta$ -dimethyl- $\alpha\gamma$ -pentadiene is obtained.

δ -Hydroxy- $\beta\delta\zeta$ -trimethyl- $\beta\epsilon$ -heptadiene,



from phorone and magnesium methyl iodide, forms white needles melting at 57.5° and boiling at 43 — 46° under 0.25 mm. pressure. It is without odour when solid, but has an intense camphor-like odour when fused. The alcohol rapidly absorbs oxygen, forming a syrupy compound, $\text{C}_{10}\text{H}_{18}\text{O}_3$, with an odour of peppermint.

When distilled from sodium under 14 mm. pressure, the alcohol passes into trimethylheptatriene [$\beta\zeta$ -dimethyl- δ -methylene- $\beta\epsilon$ -heptadiene], $\text{CMe}_2\cdot\text{CH}\cdot\text{C}(\text{CH}_3)\cdot\text{CH}\cdot\text{CMe}_2$, boiling at 55 — 57° . C. H. D.

Action of Hydrogen Chloride on Aqueous Formaldehyde and Trioxymethylene. FRANZ M. LITTERSCHEID and K. THIMME (*Annalen*, 1904, 334, 1—49).—The investigations hitherto made on the action of hydrogen chloride on formaldehyde are contradictory, and have been repeated and amplified in this communication.

When hydrogen chloride is passed into a solution of commercial formalin containing methyl alcohol, chloromethyl ether, dichloromethyl ether, dichlorotrioxymethylene, and dichlorotetraoxymethylene are produced (compare Litterscheid, *Abstr.*, 1901, i, 443; and Sonay, *Bull. Acad. roy. Belg.*, 1894, 28, 629). The four substances can be isolated and recognised by the aid of their trimethylamine additive products.

In the absence of methyl alcohol, dichloromethyl ether and dichlorotrioxymethylene, together with dichlorotetraoxymethylene, are formed. It is also shown that, in the action of hydrogen chloride on commercial formalin or pure formaldehyde solution, the compounds obtained by Lösekann (*Abstr.*, 1892, 423) and Coops (*Abstr.*, 1902, i, 77), chloromethyl alcohol, hydroxychloromethyl ether, and hydroxychlorotrioxymethylene, do not appear to exist. Similarly, the chloromethyl alcohol of Grassi-Cristaldi and Maselli (*Abstr.*, 1898, i, 294) is dichlorotrioxymethylene.

The formaldehyde solution used contained 37.1 per cent. of formaldehyde and a small quantity of acetone. The methyl alcohol was estimated by treating the solution with $1\frac{1}{2}$ volumes of 10 per cent. ammonia, then acidifying and distilling, and determining the sp. gr. of the distillate; it amounted in this specimen to 12 per cent., in the "Formal I" of the Farbwerke vorm. Meister, Lucius, & Brüning to 18 per cent., and in another commercial preparation to 11 per cent.

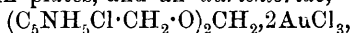
The commercial formalin was saturated at 0° with dry hydrogen chloride, when an oily liquid separated, after repeated fractionation, this liquid was divided into four fractions: a large fraction, *A*, boiling at 58.5—62°; a small fraction, *B*, boiling at 70—100°; a second large fraction, *E*, boiling at 100.5—101.5°; and another small fraction, *D*, boiling at 91—92°. These fractions were treated in ethereal solution with trimethylamine and the resulting additive products studied in the form of their platinum and gold salts.

Fraction *A* consisted only of chloromethyl ether; the *additive* product with trimethylamine, $\text{OMe}\cdot\text{CH}_2\cdot\text{NMe}_3\text{Cl}$, forms crystals, and the *platinichloride*, $(\text{OMe}\cdot\text{CH}_2\cdot\text{NMe}_3\text{Cl})_2\cdot\text{PtCl}_4$, crystallises in brownish-red prisms melting at 228—229°. Fraction *B* is a mixture of chloro- and dichloro-methyl ether. The *additive* product with trimethylamine is treated in aqueous solution with platinic chloride, when the *platinichloride* of the dichloro-compound, $\text{O}(\text{CH}_2\cdot\text{NMe}_3\text{Cl})_2\cdot\text{PtCl}_4\cdot\text{H}_2\text{O}$, crystallises in four-sided leaflets melting at 241°; the *platinichloride* of the monochloro-compound remains in the mother liquor. Fraction *D* also contains these two compounds. Fraction *E* consists only of dichloromethyl ether.

The residue boiling above 103° was fractionated and yielded: fraction *F*, which contained, besides dichloromethyl ether, dichlorotrioxymethylene, the trimethylamine *additive* product of which yields a *platinichloride*, $(\text{NMe}_3\text{Cl}\cdot\text{CH}_2\cdot\text{O})_2\text{CH}_2\cdot\text{PtCl}_4$, which forms rhombic crystals.

tals melting at 235—240°. Fraction *G*, boiling above 117°, contained mainly dichlorotetraoxymethylene, the trimethylamine additive product of which yielded a *platinichloride*, $(\text{NMe}_3\text{Cl}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2)_2\text{O}\cdot\text{PtCl}_4$, a pale yellow precipitate. Dichloromethyl ether and dichlorotrioxymethylene were also probably present in this fraction. Fraction *II*, boiling above 125°, consists mainly of dichlorotetraoxymethylene, the trimethylamine *additive* product of which yields an *aurichloride*, $(\text{NMe}_3\text{Cl}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2)_2\text{O}\cdot 2\text{AuCl}_3$, melting at 204°. It is claimed that these results show that Coops' observations (*loc. cit.*) are incorrect.

A solution of formaldehyde free from methyl alcohol was obtained by distilling trioxymethylene in a copper retort and collecting the distillate in water. The product of the action of hydrogen chloride on this solution was treated in the same manner as above described. Dichloromethyl ether, dichlorotrioxymethylene, and dichlorotetraoxymethylene were isolated. The dichlorotrioxymethylene is identical with Sonay's dichloromethylal, which was obtained by chlorinating methylal. The additive compound of the trioxymethylene with pyridine was prepared from the substance obtained from both sources and converted into a *platinichloride*, $(\text{C}_5\text{NH}_5\text{Cl}\cdot\text{CH}_2\cdot\text{O})_2\text{CH}_2\cdot\text{PtCl}_4$, which crystallised in plates, and an *aurichloride*,



crystallising in needles.

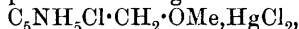
A repetition of Grassi-Cristaldi and Maselli's experiments on the action of hydrogen chloride on trioxymethylene at 180°, in which they stated chloromethyl alcohol was formed, showed that only dichloromethyl ether and dichlorotrioxymethylene were produced.

Determinations of the molecular weight of formaldehyde in dilute aqueous solution showed that formaldehyde was partly present in a polymeric form, probably trioxymethylene, a result previously obtained by Tollens and Kraut for more concentrated solutions.

K. J. P. O.

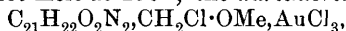
Reactions of Chloromethyl Alkyl Ethers. FRANZ M. LITTERSCHEID and K. THIMME (*Annalen*, 1904, 334, 49—67. Compare preceding abstract).—As a means of recognising and isolating the substituted methyl ethers described in the preceding abstract, the reaction of these compounds with organic bases has been investigated.

Chloromethyl ether is best prepared by treating trioxymethylene with methyl-alcoholic hydrogen chloride and then passing in hydrogen chloride until solution is complete; the ether is then rectified. The *picrate*, $\text{OMe}\cdot\text{CH}_2\cdot\text{NMe}_3\cdot\text{O}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$, crystallises in dark yellow needles melting at 198°. The ether unites with pyridine in ethereal solution, the *additive* product forming a *mercurichloride*,

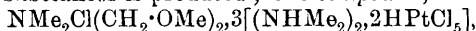


which crystallises in four-sided plates melting at 91°. In the absence of a diluent, pyridine decomposes the chloro-ether, pyridine hydrochloride being formed. Chloromethyl ether and quinoline yield an *additive* product in the presence of chloroform, the *platinichloride* of which, $(\text{C}_9\text{NH}_7\text{Cl}\cdot\text{CH}_2\cdot\text{OMe})_2\cdot\text{PtCl}_4$, crystallises in rhombic plates melting at 232—234°; the *aurichloride*, $\text{C}_9\text{NH}_7\text{Cl}\cdot\text{CH}_2\cdot\text{OMe}\cdot\text{AuCl}_3$, forms

golden-yellow, rhombic plates melting at 126—127°. The *additive* compound with strychnine, $C_{21}H_{22}O_2N_2 \cdot CH_2Cl \cdot OMe$, forms leaflets; its *platinichloride*, $(C_{21}H_{22}O_2N_2 \cdot CH_2Cl \cdot OMe)_2 \cdot PtCl_4$, forms brown crystals which do not melt at 250°; the *aurichloride*,



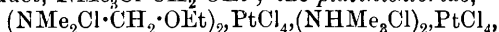
crystallises in needles melting at 193°. The *additive* compound with narcotine, $C_{22}H_{23}O_7N \cdot CH_2Cl \cdot OMe$, crystallises in leaflets melting and decomposing at 210° and is decomposed on treatment with gold chloride. The *additive* compound with hexamethylenetetramine, $C_6H_{12}N_4 \cdot CH_2Cl \cdot OMe$, is decomposed by gold chloride, the *aurichloride* of hexamethylenetetramine, $C_6H_{12}N_4 \cdot HAuCl_4$, being formed and crystallising in golden-yellow needles melting at 192°. The *additive* compound with cytosine was only isolated in the form of the gold salt, $C_{11}H_{14}ON_2 \cdot CH_2Cl \cdot OMe \cdot AuCl_3$, which forms crystals melting and decomposing at 202°. The *additive* product with dimethylamine is hygroscopic and yields an *aurichloride*, $NMe_2Cl(CH_2 \cdot OMe)_2 \cdot AuCl_3$, which crystallises in leaflets melting at 86—88°, and is not a simple *additive* product, but a quaternary base. The *platinichloride*, $[NMe_2Cl(CH_2 \cdot OMe)_2]_2 \cdot PtCl_4$, is obtained from the *aurichloride* and crystallises in rhombic plates melting at 197°. If the aqueous solution of the *additive* product is directly treated with platinic chloride, a mixture of substances is produced; one compound,



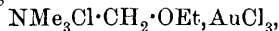
crystallises in rosettes melting at 212—214°; another compound, $NMe_2Cl(CH_2 \cdot OMe)_2 \cdot PtCl_4 \cdot 2[(NHMe_2)_2 \cdot H_2PtCl_6]$, crystallises in needles melting at 202—204°.

Chloromethyl ether forms both with phenol and aniline amorphous insoluble condensation products.

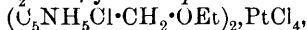
Chloromethyl ethyl ether forms with trimethylamine a crystalline *additive* product, $NMe_3Cl \cdot CH_2 \cdot OEt$; the *platinichloride*,



is a yellow salt melting at 226°. The *aurichloride*,

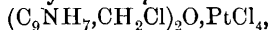


crystallises in leaflets melting at 139°. The normal *platinichloride*, $(NMe_3Cl \cdot CH_2 \cdot OEt)_2 \cdot PtCl_4$, can be prepared from the *aurichloride* and crystallises in leaflets melting at 230°. The *additive* product with pyridine, $C_5NH_5Cl \cdot CH_2 \cdot OEt$, yields a *platinichloride*,



crystallising in plates which melt at 178°; the *aurichloride*, $C_5NH_5Cl \cdot CH_2 \cdot OEt \cdot AuCl_3$, crystallises in leaflets melting at 87—88°.

Dichloromethyl ether forms an *additive* product with quinoline, $(C_9NH_7 \cdot CH_2Cl)_2O$, which yields a *platinichloride*,



crystallising in needles melting at 232°; the *aurichloride*, $(C_9NH_7 \cdot CH_2Cl)_2O \cdot AuCl_3$, crystallises in needles which do not melt at 250°. The *additive* compounds of this ether are more stable than those of chloromethyl ether.

K. J. P. O.

Action of Methyl Sulphate on Sodium Hyposulphite.
ARTHUR BINZ (*Ber.*, 1904, 37, 3549—3550. Compare Bernthsen and

Bazlen, Abstr., 1900, ii, 203).—*Methyl sodium thiosulphate* is formed when methyl sulphate and sodium hyposulphite are warmed together for a few minutes at 70° and the product extracted with boiling alcohol. If the heating is continued at 70° or at a higher temperature in a reflux apparatus, sulphur dioxide, methyl sulphide, and methyl disulphide are evolved, and on heating to 200° a sublimate of dimethylsulphone is formed. G. Y.

Electrolysis of Potassium Acetate. FRITZ FOERSTER and A. FIGUET (*Zeit. Elektrochem.*, 1904, 10, 729—736).—When an aqueous solution of potassium acetate is electrolysed with a smooth platinum anode, the principal reaction is $2\text{KC}_2\text{H}_3\text{O}_2 + 2\text{H}_2\text{O} = \text{H}_2 + 2\text{KOH} + \text{C}_2\text{H}_6 + 2\text{CO}_2(1)$. In addition to this, acetic acid may be oxidised to carbon dioxide or to carbon monoxide, $\text{CH}_3\cdot\text{CO}_2\text{H} + 4\text{O} = 2\text{CO}_2 + 2\text{H}_2\text{O}(2)$ and $\text{CH}_3\cdot\text{CO}_2\text{H} + 2\text{O} = 2\text{CO} + 2\text{H}_2\text{O}(3)$, or free oxygen may be formed. The authors find that an iridium anode gives the same products as one of smooth platinum. With platinised platinum, carbon dioxide and oxygen are the main products; a little carbon monoxide is also formed, but no ethane, unless the anode has first been anodically polarised in a solution of sodium hydroxide. Iron and palladium behave in the same way as unpolarised platinised platinum. It appears that the different behaviour of the metals is connected with the varying potentials at which oxygen is liberated at them, the potential required for the formation of ethane lying below that at which oxygen is evolved at platinum or iridium anodes, but above the value for iron or palladium anodes.

The variations of *E.M.F.* observed during the electrolysis are also discussed at some length, but no definite result is arrived at.

T. E.

Measurements of Conductivity of Unsaturated Acid. FRITZ FICHTER and ALFRED PFISTER (*Annalen*, 1904, 334, 201—210).—Redetermination of the dissociation-constant of vinylacetic acid has shown that the number previously recorded (Abstr., 1902, i, 256) is erroneous, and that the mean value of *K* is 0.00383. This number is twice as large as that observed by Ostwald for crotonic acid, *K* = 0.00204. This is the first recorded instance of a pair of unsaturated acids differing only in the position of the double linking, in which the $\beta\gamma$ -unsaturated acid possesses a higher degree of dissociation than the $\alpha\beta$ -acid. A series of unsaturated isomeric acids, differing only in the position of the double linking, have been investigated, and it has been demonstrated that the dissociation constant of the $\beta\gamma$ -acid always is distinctly higher than that of the $\alpha\beta$ -acid. This rule holds both for aliphatic and cyclic compounds, and is solely dependent on the relative positions of the double linking and the carboxyl group. If the double linking is in the $\gamma\delta$ - or in the $\delta\epsilon$ -positions relative to the carboxyl group, there appears to be a regular decrease of the dissociation coefficient.

The following table gives a summary of the results :

| | | | |
|---|---------|---------------------------------------|---------|
| Butyric acid | 0·00154 | Valeric acid | 0·00161 |
| Crotonic acid | 0·00204 | $\alpha\beta$ -Pentenoic acid..... | 0·00148 |
| Vinylacetic acid | 0·00383 | $\beta\gamma$ -Pentenoic acid..... | 0·00335 |
| | | $\gamma\delta$ -Pentenoic acid | 0·00209 |
| α -Methyl- $\alpha\beta$ -pentenoic acid | 0·00097 | Hexoic acid | 0·00146 |
| α -Methyl- $\beta\gamma$ -pentenoic acid | 0·00299 | $\alpha\beta$ -Hexenoic acid | 0·00189 |
| α -Methyl- $\gamma\delta$ -pentenoic acid | 0·00216 | $\beta\gamma$ -Hexenoic acid | 0·00264 |
| | | $\gamma\delta$ -Hexenoic acid | 0·00174 |
| | | $\delta\epsilon$ -Hexenoic acid | 0·00191 |

From these results, it follows that the $\alpha\beta$ unsaturated acids are feebler acids than would be expected from the negative character of the double linking and the greater influence of α -substituents on the affinity constants of acids. This fact is accounted for, by the help of Thiele's theory of partial valencies. In the case of the $\alpha\beta$ -unsaturated acids, a conjugated system of double linkings is present, and as a consequence the system is less unsaturated than in the case of the $\beta\gamma$ - or $\gamma\delta$ unsaturated acids, thus: $C:C:C:C:O$ and $C:C\cdot C:C:O$.



K. J. P. O.

Acetyl Derivative of Fermentation Lactic Acid. RICHARD ANSCHÜTZ and W. BERTRAM (*Ber.*, 1904, 37, 3971—3974).—Acetyl-*i*-lactic acid, $OAc\cdot CHMe\cdot CO_2H$, prepared by the action of acetyl chloride on *i*-lactic acid, melts indefinitely at $57-60^\circ$, boils at 127° under 11 mm. pressure, and is deliquescent. The action of water on it at various temperatures was investigated; at the ordinary temperature it is slowly hydrolysed, whilst at $150-160^\circ$ for five hours it is completely hydrolysed. *Acetyl-lactyl chloride* boils at 56° under 11 mm. pressure and at 150° under 760 mm. pressure. It has sp. gr. 1·1920 at $17\frac{1}{4}^\circ$ and n_D 1·4241 at 17° .

Guaiacol acetyl-lactate, $OAc\cdot CHMe\cdot CO_2\cdot C_6H_4\cdot OMe$, prepared by heating acetyl-lactic acid chloride with guaiacol until the evolution of hydrogen chloride ceases, melts at 71° and boils at 180° under 13 mm. pressure. It separates from ether, chloroform, or benzene in pyramids.

Acetyl-lactylanilide, prepared by the action of acetyl-lactic acid chloride on an ethereal solution of aniline, separates from dilute alcohol in silky needles and melts at $121-122^\circ$.

Acetyl-lactylphenetide separates from water in glistening needles and melts at 129° .

Acetyl-lactonitrile, prepared by the action of acetyl chloride on lactonitrile, boils at 73° under 8 mm. pressure and at $172-173^\circ$ under 760 mm. pressure.

A. McK.

Lactonic Acids, Lactones, and Unsaturated Acids. RUDOLF FITTIG (*Annalen*, 1904, 334, 68—143).—In this paper, a number of observations are collected which complete and amplify the researches already carried out in this field.

I. *Isomeric Hydroxyvalerolactones*.—[With ERICH LEPÈRE.]—In the transformation of α -hydroxy-acids into α - and γ -ketonic acids, hydroxy-lactones are supposed to be formed as intermediate products; thus a hydroxyvalerolactone is formed in the transformation of α -hydroxypentenoic acid. The constitution of this lactone is uncertain, and has consequently been reinvestigated.

α -Hydroxyvalerolactone is synthesised by preparing the nitrile, $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CN}$, by adding molecular quantities of potassium cyanide and hydrochloric acid to an ethereal solution of freshly distilled aldol cooled to -10° ; the nitrile is obtained as an oil contaminated with small quantities of the aldol, and *isodialdan* (m. p. $113-114^\circ$). The crude nitrile was converted by treatment with concentrated hydrochloric acid in ethereal solution into the *lactone*, which was purified by means of the calcium salt of the dihydroxyvaleric acid, and forms a colourless neutral liquid. *Calcium α -dihydroxyvalerate*, $(\text{C}_5\text{H}_9\text{O}_4)_2\text{Ca}$, and the *barium* salt are amorphous, hygroscopic powders; the *zinc* salt crystallises in prisms.

When the calcium salt of $\alpha\gamma$ -hydroxyvaleric acid is boiled with dilute hydrochloric acid, a lactone, *isohydroxyvalerolactone*, isomeric with α -hydroxyvalerolactone, is formed; it can readily be separated from the α -compound by conversion into the calcium salt of the dihydroxy-acid, which differs from the calcium salt of the $\alpha\gamma$ -dihydroxy-acid corresponding with the α -hydroxylactone by being insoluble in alcohol. After five hours' boiling, 50 per cent. of the α -lactone is converted into the new compound. The latter is a thick, colourless oil. The *calcium* salt forms crystals, the *barium* salt crystallises with H_2O in needles or plates, and the *silver* salt crystallises in needles which are converted into leaflets by rubbing. The *isohydroxyvalerolactone* cannot be reconverted into the α -hydroxy-compound; when the calcium salt is boiled with hydrochloric acid, l  vulic acid is alone produced.

The third hydroxyvalerolactone, the α -hydroxyvalerolactone prepared from α -hydroxypentenoic acid, is not identical with the α -hydroxyvalerolactone obtained from aldolcyanohydrin, since the calcium salt does not yield *isohydroxyvalerolactone* when boiled with hydrochloric acid, but is converted into l  vulic acid. The three hydroxyvalerolactones distil undecomposed; α -hydroxyvalerolactone boils at $245-260^\circ$, *isohydroxyvalerolactone* at $250-255^\circ$, and the hydroxyvalerolactone from the pentenoic acid at $240-260^\circ$. None of the compounds are volatile with water vapour.

It is suggested that in the conversion of the α -hydroxyvalerolactone into the *iso*-compound the hydroxy-group migrates from the α - to the β -position. It is probable that the *isolactone* and the lactone from the hydroxypentenoic acid are stereoisomeric.

II. *Isomeric Ethyl Crotonates*.—[With PERCY BORSTELMANN and MARK LURIE.]—When diethylglycollic acid (α -hydroxy- α -ethylbutyric acid), which is, contrary to expectation, volatile with steam, is distilled, two fractions are obtained, boiling at 150° and above 200° . Two isomeric acids can be isolated from the product by neutralising with calcium carbonate and evaporating until needles crystallise out. The crystals are more soluble in cold water than in hot; from the hot solution, which has been filtered from the one calcium salt, the other

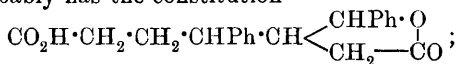
calcium salt separates. The calcium salt, which is less soluble in hot water, is the salt of *α-ethylisocrotonic acid*, $\text{CHMe}:\text{CEt}\cdot\text{CO}_2\text{H}$, which is an oily liquid, boiling at $199\cdot5^\circ$ under 750 mm. pressure and not solidifying at -19° ; the *calcium* salt crystallises with $2\text{H}_2\text{O}$ in needles. The more soluble *calcium* salt, $(\text{C}_6\text{H}_9\text{O}_2)_2\text{Ca}\cdot 5\text{H}_2\text{O}$, is the salt of the solid ethylcrotonic acid, isomeric with the acid just mentioned.

When the *iso*-acid is boiled for several hours, it is converted completely into the isomeride. On oxidising the calcium salt with permanganate at 0° , oxalic acid and a dihydroxy-acid, $\text{C}_6\text{H}_{12}\text{O}_4$, are produced; the latter is called *isohexeric acid*, and is identical with the acid previously described by Fittig and Howe (Abstr., 1880, 376) as hexeric acid, the name hexeric acid being now reserved for the product of oxidation of ethylcrotonic acid; it melts at $144\cdot5$ – 145° , and is not volatile with steam; its *calcium* salt crystallises with $2\text{H}_2\text{O}$.

It is thought that the ethylisocrotonic acid bears the same relation to ethylcrotonic acid as angelic does to tiglic acid; the calcium salts show the same differences in their solubilities, and the boiling points bear the same relation. Their behaviour towards bromine is different; whilst both angelic and tiglic acids yield the same product, dibromotiglic acid, the ethylcrotonic acids give two different compounds. The *dibromide* of ethylisocrotonic acid, prepared by the action of bromine in chloroform solution in diffused daylight, forms colourless, monosymmetric crystals melting at $116\cdot5^\circ$, and is decomposed by boiling with water or aqueous sodium carbonate into bromoamylenes and *isohexeric acid*; the *dibromide* of ethylcrotonic acid (m. p. $83\cdot5^\circ$) also yields *isohexeric acid* on heating with water. It is probable that the production of the same acid is accounted for by a transformation of the dibromoethylcrotonic acid.

β -Hydroxy- α -ethylbutyric acid, which is prepared by reduction of ethyl acetoacetate in aqueous alcoholic solution by 4 per cent. sodium amalgam and purified by means of the zinc salt, yields on distillation the same products as the α -hydroxy-acid. The *calcium* and *barium* salts are anhydrous and amorphous, the *zinc* salt crystallises with H_2O .

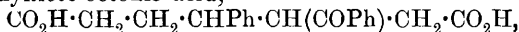
III. *Polymerisation of Phenylisocrotonic Acid*.—[With KARL HADORFF.] (Compare Abstr., 1898, i, 196.)—In continuation of previous work (*loc. cit.*), the behaviour of phenylisocrotonic acid towards hydrochloric acid of different concentrations has been tested. When heated with a mixture of one volume of concentrated hydrochloric acid and three volumes of water, phenylbutyrolactone is alone formed, but with a mixture of hydrochloric acid (1 vol.) and water (2 vols.) a small quantity of a new acid is also produced, the amount of which increases as the concentration of the hydrochloric acid increases. This new acid is formed without disturbing the equilibrium between the *isocrotonic* acid and the lactone, the reaction coming to an end when 65 per cent. of the acid has changed. The acid, which is now called diphenyloctolactonic acid, is identical with the polymeric phenylisocrotonic acid previously described (Abstr., 1885, 528; 1890, 894), and probably has the constitution



it is a monobasic acid crystallising in leaflets melting at 179° , and

yields two series of salts, in one of which the lactone ring is broken. The *calcium* salt of the lactone, $(C_{20}H_{19}O_4)_2Ca$, is crystalline, but the *barium* and *silver* salts amorphous; the *barium* and *silver* salts of the dibasic hydroxy-acid were prepared.

When oxidised with chromic acid, benzoic acid is produced together with diphenylketo-octonic acid,



which forms crystals melting at 132° and is not volatile with steam; on reduction with sodium amalgam, it is reconverted into the original lactonic acid; the *barium* salt is crystalline and the *silver* salt amorphous.

IV. *Polymerisation of Phenylbromobutyrolactone with the Elimination of Hydrogen Bromide*.—[With FRANZ STADLMAYR.]—A polymerisation similar to that described above is observed when phenylbromobutyrolactone is treated with sodium hydroxide; under the influence of dilute sodium hydroxide, benzoylpropionic acid is alone formed. When 25 per cent. sodium hydroxide is used, a solid substance, the diphenyl-octenedilactone, separates, whilst a mixture of three acids can be obtained from the solution. Benzoylpropionic acid can be extracted by carbon disulphide, and the two other acids separated by means of their calcium salts. The two acids are respectively the *diphenylketo-octolactonic acid* and the *isodiphenylketo-octolactonic acid*, and are stereoisomeric, $CO_2Na \cdot CH_2 \cdot CHBz \cdot CPh < \begin{matrix} CH_2 \cdot CH_2 \\ O - CO \end{matrix}$. The normal acid

crystallises with $3H_2O$ in needles melting at $195-197^\circ$ when anhydrous; its *calcium* salt, $(C_{20}H_{17}O_5)_2Ca \cdot 2\frac{1}{2}H_2O$, crystallising in needles, can only be prepared with difficulty, since the acid very readily passes into the corresponding hydroxy-dibasic acid, the *calcium* salt of which, $C_{20}H_{18}O_6Ca$, is amorphous. When treated in neutral solution with phenylhydrazine hydrochloride and sodium acetate, the acid yields the *anhydride* of the phenylhydrazone, $C_{26}H_{22}O_3N_2$, which forms yellow crystals softening at 50° and decomposing at 70° .

isoDiphenylketo-octolactonic acid crystallises in prisms melting at $202-206^\circ$ and is more stable towards calcium hydroxide than the isomeride, being converted only after heating for several hours into the dibasic hydroxy-acid; the *calcium* salt is anhydrous and crystallises in needles, whilst the *calcium* salt of the dibasic acid is amorphous.

Diphenyloctenedilactone, $\begin{matrix} CO-O \\ | \\ CH_2-CH_2 \end{matrix} > CPh \cdot C < \begin{matrix} CPh-O \\ CH_2-CO \end{matrix}$, obtained as

just described, crystallises in needles, decomposing at 210° and melting at $226-227^\circ$; by alkali hydroxides it is converted into diphenylketooctolactonic acid, together with a very small quantity of an isomeric acid, $C_{20}H_{18}O_5$, which is separated by means of its calcium salt and melts at $170-171^\circ$; it behaves as a monobasic lactonic acid.

K. J. P. O.

Camphorcarboxylic Acid, its Salts, Esters, and Ester Salts.
II. JULIUS W. BRÜHL and H. SCHRÖDER (*Ber.*, 1904, 37, 3943-3958. Compare this vol., i, 646).—Spectrochemical investigation showed that camphorcarboxylic esters are pure ketonic compounds at the ordinary temperature, whereas their acyl derivatives are pure enolic

compounds and their alkyl derivatives pure ketonic compounds. In such cases, therefore, compounds which are capable of exhibiting tautomerism are obtained as liquids, which do not consist of a mixture of the allelotropic forms.

Solutions of the ester salts in various alcohols are stable and suitable for spectrochemical measurement, although aqueous solutions of such salts are unsuitable owing to the autohydrolysis which they undergo. Sodium was dissolved in a definite amount of a given alcohol and the equivalent amount of ester added, the methyl ester being used with sodium methoxide, the ethyl ester with sodium ethoxide, and so on. This solution was then optically investigated, as were also the corresponding alcohol, sodium alkylxide, and homogeneous ester.

The data obtained for the molecular refraction of the dissolved ester gave, in every case, numbers higher than those observed for the homogeneous ester. The conclusion is drawn that camphorcarboxylic esters suffer enolisation during salt formation, and that the salts thus formed are enolic compounds.

At high concentrations, the groups in the dissolved ester salts are in the same physical and chemical condition in all solvents. The values obtained for solutions in methyl and ethyl alcohols vary with the concentration, whilst the latter influence has little effect when amyl alcohol is used.

The chemical behaviour of solutions of camphorcarboxylic acid and its derivatives in various solvents is discussed. Camphorcarboxylic acid, its salts, and its ester salts exist in solution sometimes in the unimolecular and sometimes in the polymolecular form according to the particular solvent used. All the unimolecular forms react with alkyl haloids, but none of the polymolecular forms do so. A. McK.

Glyoxylic Acid. HANS MEYER (*Ber.*, 1904, 37, 3591—3592. Compare Tafel and Friedrichs, this vol., i, 849).—*Methyl glyoxylate*, prepared by electrolytic reduction of methyl oxalate, crystallises from methyl formate in colourless leaflets, melts at 53°, and volatilises readily at the ordinary temperature. The *phenyl-methylhydrazone* forms silvery leaflets, melts at 158—160°, and dissolves readily in alcohol. The *p-nitrophenylhydrazone* crystallises from acetone or pyridine in small, yellow needles and chars at 170—180°. C. H. D.

Convenient New Method of preparing Normal Pimelic Acid. JULIUS VON BRAUN (*Ber.*, 1904, 37, 3588—3591. Compare Hamonet, this vol., i, 643).—On warming a solution of crude α -dichloro- or dibromo-pentane (this vol., i, 841, 918) with potassium cyanide, pimelonitrile, $C_5H_{10}(CN)_2$, is obtained as a colourless, odourless liquid, boiling at 171—172° under 12 mm. pressure and yielding pimelic acid on hydrolysis.

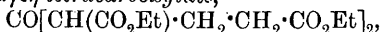
Since α -dichloropentane is prepared from piperidine, and calcium pimelate yields cyclohexanone on distillation, this reaction affords a means of passing from a secondary cyclic base to a cyclic ketone. C. H. D.

Action of Nitric Acid on Ethyl Acetonedicarboxylate. CELSO ULPANI and L. BERNARDINI (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 331—335).—By the action of fuming nitric acid charged with nitrous vapours on ethyl acetonedicarboxylate, Henry and von Pechmann (Abstr., 1893, i, 397) obtained a compound described by them as the peroxide of ethyl dinitrosoacetonedicarboxylate. The authors find that this compound is accompanied by a nitrogenated oil, which can also be obtained as the sole product of the action of nitric acid, free from nitrous fumes, on ethyl acetonedicarboxylate. This oil is found to be identical with the peroxide of ethyl oximinoacetate obtained by the action of fuming nitric acid on ethyl acetoacetate.

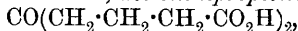
When treated with concentrated ammonia solution, the oil is quantitatively transformed into a compound, $(\text{CHON})_n$, which is identical with the product obtained by Steiner (Abstr., 1876, ii, 288) from concentrated sulphuric acid and ammonium fulminurate and with the compound obtained by the action of concentrated sulphuric acid on nitromalonamide (Ulpiani and Ferretti, Abstr., 1902, i, 430).

T. H. P.

Acetonedipropionic Acid and its Derivatives. HANS VON PECHMANN and NEVIL V. SIDGWICK (*Ber.*, 1904, 37, 3816—3829).—*Ethyl ketoheptane- α - γ -tetracarboxylate*,

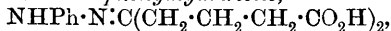


is readily obtained by the action of sodium ethoxide on ethyl acetonedicarboxylate and ethyl β -iodopropionate. It distils at 220—230° under 12 mm. pressure, but considerable loss results owing to decomposition. When the crude ester is hydrolysed with moderately concentrated hydrochloric acid, *acetonedipropionic acid*,



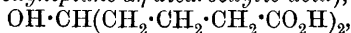
is obtained. This exists in two modifications, which, so far, have not been transformed into each other. The one crystallises from water or from a mixture of chloroform and light petroleum in nodular aggregates melting at 101—102°. It gives no coloration with ferric chloride and is readily soluble in most solvents. *Barium, sodium, copper, silver, zinc, and lead* salts have been prepared.

The second modification is insoluble in chloroform, crystallises from hot water in plates melting at 108—109°, and forms only about 20 per cent. of the mixture. Both acids yield the same derivatives. The *dimethyl* ester crystallises from light petroleum in colourless plates melting at 30—31°. The *phenylhydrazine*,



crystallises from dilute alcohol in colourless needles which turn brown on exposure to the air and completely decompose when kept. It melts and decomposes at 151°, is insoluble in benzene or light petroleum, and does not give Bülow's reaction. The *semicarbazone*, $\text{C}_{10}\text{H}_{17}\text{O}_5\text{N}_3$, crystallises from hot water in thick prisms and melts and decomposes at 180—181° when rapidly heated.

On reduction with sodium amalgam, the ketonic acid yields *hydroxy-azelaic acid* (δ -hydroxyheptane- α - γ -dicarboxylic acid),



which may be purified by aid of its *barium* salt, $C_9H_{14}O_5Ba, 4H_2O$. The acid crystallises from chloroform or benzene in small plates melting at $104-105^\circ$, and on further reduction with fuming hydriodic acid yields a small amount of azelaic acid.

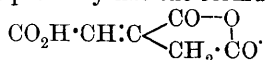
Acetic anhydride has no action on the ketonic acid (compare Volhard, Abstr., 1892, 432), but when heated alone water is eliminated and a mixture of unaltered acid and 1:3-diketocyclohexane-2-propionic acid, $CH_2<\begin{smallmatrix} CH_2 \cdot CO \\ CH_2 \cdot CO \end{smallmatrix}>CH \cdot CH_2 \cdot CH_2 \cdot CO_2H$, is obtained. The new acid crystallises from water in well-developed prisms which sinter at 170° and melt at $180-181^\circ$. It possesses all the characteristics of the dihydroresorcinol derivatives (Merling, Abstr., 1894, i, 177; Volhard, *ibid.*, 1897, i, 422). Its *dioxime*, $C_9H_{14}O_4N_2$ forms colourless, rhombic plates, which turn brown at 200° and melt at $203-206^\circ$. With semicarbazide, it yields a compound, $C_{11}H_{16}O_3N_6$, which melts and decomposes at 278° ; in composition, this corresponds with a disemicarbazone minus a molecule of water. Its reaction with phenylhydrazine is complex, and a red, crystalline compound is obtained which gives a deep blue coloration with mineral acids. Nitrous acid reacts with the diketocyclohexanepropionic acid producing a rupture of the ring, and thus yielding γ -isonitroso- δ -ketoheptane- $\alpha\gamma$ -dicarboxylic acid, $CO_2H \cdot CH_2 \cdot CH_2 \cdot C(N \cdot OH) \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$, which forms pale yellow crystals melting and decomposing at $133-136^\circ$. It does not give the Liebermann reaction, and when warmed with concentrated sulphuric acid and poured on to ice (Beckmann's transformation) it yields glutaric and succinic acids, and hence has the above constitution.

Succinic acid diphenylhydrazide melts at $209-211^\circ$ J. J. S.

Anhydroaconitic Acid. RICHARD ANSCHÜTZ and W. BERTRAM (*Ber.*, 1904, 37, 3967-3970. Compare Abstr., 1903, i, 550).—By the action of acetyl chloride on aconitic acid, Easterfield and Sell (*Trans.*, 1892, 61, 1009) obtained an anhydride of aconitic acid. Anhydroaconitic acid, prepared by the action of a chloroform solution of acetyl chloride on aconitic acid, crystallises in octahedra and melts at 76° . When prepared as described by Easterfield and Sell, it also melts at 76° and not at 95° as stated by those authors. The same substance, melting at 76° , may also be obtained by heating aconitic acid at 140° under 15-20 mm. pressure. When an attempt was made to distil anhydroaconitic acid under diminished pressure, carbon dioxide was evolved and itaconic anhydride formed.

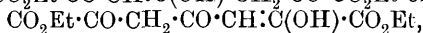
When anhydroaconitic acid is quickly heated at 250° under the ordinary pressure, the distillate contains a mixture of itaconic and citraconic anhydrides.

Anhydroaconitic acid probably has the formula

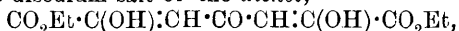


Anhydromethylocitric acid [*anhydromethoxytricarballic acid*], prepared by the action of acetyl chloride on methoxytricarballic acid, separates in prisms and melts at 131° . A. McK,

Ethyl Acetonedioxalate (Desmotropy and the Origin of Colour). RICHARD WILLSTÄTTER and RUDOLF PUMMERER (*Ber.*, 1904, 37, 3733—3740).—The authors prepare ethyl acetonedioxalate by condensing acetone directly with two mols. of ethyl oxalate, instead of isolating, as in Claisen's method, the ethyl sodioacetoneoxalate formed as an intermediate product; in this way, a yield of 78 per cent. that of theory can be obtained. The principal product of the synthesis is the monoenol, $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{CH}\cdot\text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ or



which forms nearly colourless crystals, melts at 104° , and has a solubility of 1.6 grams in 100 c.c. of ether. When the monoenol is dissolved in alcohol and sodium hydroxide is added, a crystalline precipitate of the disodium salt of the *dienol*,



is obtained; on treating this with less than the calculated quantity of dilute hydrochloric acid, the dienol itself is obtained, melting at 97.5 — 98.5° . It differs from the monoenol in being yellow and in having pronounced tinctorial properties; it absorbs ammonia vapour to form a *diammonium* salt. The monoenol and the dienol are isodynamic and exist together in different equilibria in different solvents; a drop of water added to the colourless alcoholic solution of the monoenol gives rise to the yellow colour of the dienol. On heating either the aqueous or alcoholic solution of the monoenol, an increase in the colour is produced, showing an increase in the proportion of the dienol present. Traces of alkali increase in a marked manner the amount of the dienol existing in solution, whilst acids destroy the latter and remove its colour.

On boiling ethyl acetonedioxalate for 15 minutes with absolute alcohol, it is converted very largely into ethyl chelidonate, which is best prepared by this method.

W. A. D.

Action of Formaldehyde on Inorganic Compounds. LUDWIG VANINO and LORENZ SEEMANN (*Chem. Centr.*, 1904, ii, 1205; from *Pharm. Centr.-II.*, 45, 733—735).—By the action of a solution of formaldehyde (3 mols.) on nitric acid (4 mols.), nitric oxide (4 mols.), carbon dioxide (3 mols.), and water are formed, and by this means nitrous vapours may be rapidly prepared; a small quantity of nitrogen is also formed by secondary actions. When solid ammonium nitrate is heated with paraformaldehyde, nitrogen is liberated in abundance, together with small quantities of nitric oxide; the former results from the action of the aldehyde on nitrous oxide, formic acid being also formed. Nitrous oxide, however, is not attacked by formaldehyde in the cold. Hexamethylenetetramine is not acted on by nitric acid at first, but after a time it becomes yellow, and on prolonged heating it is suddenly decomposed with liberation of nitric oxide. When a 40 per cent. solution of formaldehyde is poured into hot concentrated sulphuric acid, carbon separates at about 90° . When the mixture is kept cold, however, paraformaldehyde is formed, the best yield being obtained with a proportion of 10 of sulphuric acid to 50 of formaldehyde. Paraformaldehyde is also formed by the action

of pyrosulphuric acid. When phosphoric oxide is added to a 40 per cent. solution of formaldehyde, the temperature rises and carbon is formed, but by dissolving phosphoric oxide in a solution of formaldehyde, paraformaldehyde is obtained. E. W. W.

A New Anhydride of Dulcitol. P. CARRÉ (*Compt. rend.*, 1904, 139, 637—639. Compare Abstr., 1903, i, 307; this vol., i, 16, 819).—*Dulcide*, $C_6H_{10}O_4$ or $C_4H_6O_2(CH\cdot OH)_2$, an isomeride of mannide obtained by the prolonged action of phosphoric acid on dulcitol in a vacuum at a temperature of 135° , is an optically inactive, yellow liquid, boiling at 198° under 18 mm. pressure, is very hygroscopic, but does not regenerate dulcitol on treatment with water in a sealed tube at 200° , is readily soluble in alcohol or pyridine, and insoluble in ether. *Dulcide diphenylcarbamate*, $C_6H_8O_4(CO\cdot NHPh)_2$, obtained by the action of phenylcarbimide on dulcide in pyridine solution, crystallises in white plates melting at 233° . *Dulcide dibenzoate*, $C_6H_8O_4Bz_2$, similarly prepared, crystallises from alcohol in white needles melting at 138° . Dulcide is less readily esterified by phosphoric acid than mannide; the monophosphoric ester forms a barium salt containing 1 mol. of H_2O , a normal *brucine* salt crystallising with $10H_2O$, and a basic *quinine* salt containing 1 mol. of H_2O . M. A. W.

Hydration of Lactose in Solution. C. S. HUDSON (*J. Amer. Chem. Soc.*, 1904, 26, 1065—1082. Compare Abstr., 1903, ii, 623).—When a solution of lactose hydrate is evaporated at a temperature above 95° , anhydrous lactose, $C_{12}H_{22}O_{11}$, separates in large crystals, whilst at the ordinary temperature the hydrate, $C_{12}H_{22}O_{11}\cdot H_2O$, is obtained. When a large excess of the hydrate is shaken with water for a few minutes, a solution is formed the concentration of which, termed the "initial solubility," is independent of the quantity of solid substance used. On continuing the agitation for a longer period at 0° , the concentration of the solution slowly increases from 14.80 millimols. per 100 grams of water, the "initial solubility," at a constantly diminishing rate, to 34.82, the "final solubility," at which it remains constant. At this limiting value, the solution contains that quantity of anhydrous lactose which is in equilibrium with the constant quantity of hydrate, corresponding with the "initial solubility," which the solution always contains. When a substance exhibits a rate of solution, the "maximum rate of solution," independent of contact between the solid and liquid phases, and shows an initial and final solubility, it is possible to derive the velocity and equilibrium of the chemical change taking place in the solution even in cases where the substances involved cannot be separately estimated by any chemical or physical method.

Determinations have been made of the maximum rate of solution of lactose hydrate at 0° , 15° , and 25° , and the results correspond with those required by the law of mass action. The rate of hydration is increased 2.8 times by a rise of temperature of 10° . The rate of solution is greatly accelerated by bases; by the use of $N/1000$ ammonia, the velocity is increased 2.4 times. If $N/10$ ammonia solution is used instead of water, the rate of the hydration reaction is

accelerated to such an extent that the final solubility of the anhydrous sugar can be obtained in a few minutes.

The equilibrium ratio of anhydrous to hydrated lactose was calculated from the initial and final solubilities of the hydrate and was found to be 1.35 at 0°, 1.44 at 15°, and 1.51 at 25°, the degree of hydration decreasing considerably with rise of temperature. The velocity constants of the reactions of hydration and dehydration have been calculated from solubility data and also from the rate of change of optical rotation, concordant values being obtained. The amount of lactose which undergoes hydration and dehydration in one hour in a solution which has reached equilibrium has been calculated from the velocity constant and found to be 1.5 per cent. at 0° and 22.2 per cent. at 25° of the total quantity present.

The method of studying the equilibrium of dissolved substances by the principle of the maximum rate of solution is applicable to any kind of reaction which proceeds slowly in solution. Experiments have been carried out on the rate of solution of barium nitrate, potassium sulphate, sodium chloride, and iodine in water at 0°, of iodine in alcohol and in ether at 0°, and of arsenious oxide in water at 25°. There is no evidence that any slow chemical change takes place during the solution of these substances. It is shown that the slow rate of solution of arsenious oxide is not due to any chemical reaction, but is dependent on the surface of contact between the solid and the solution. It seems probable that under ordinary conditions the oxide comes into contact with the water very slowly on account of a film of air adhering to its surface.

E. G.

Rhodoose and Fucose as Antipodal Isomerides. EMIL VOTOČEK (*Ber.*, 1904, 37, 3859—3862. Compare Abstr., 1900, i, 332; 1901, i, 368; 1903, i, 67; Müther and Tollens, this vol., i, 226).—The phenylosazone of fucose has been prepared and is found to melt at 177—177.5° and not at 158—159° (Tollens). *Rhodoic acid phenylhydrazide* melts at 206°. There can be no doubt but that fucose and rhodoose are optical antipodes, and this has been confirmed by combining the two to form a *racemic compound*. This melts at 161° and is much less soluble in water than the optical isomerides (ratio of solubilities 1:5.4). Its phenylosazone melts at 187°.

Rhodoose is also obtained when convolvulin is hydrolysed with 10 per cent. sulphuric acid under slightly increased pressure.

J. J. S.

Oxidation Products of Parasaccharin. HEINRICH KILIANI and PETER LOEFFLER (*Ber.*, 1904, 37, 3612—3616. Compare this vol., i, 373).—When parasaccharin is heated for seven hours at 45—55° with dilute nitric acid, it is converted into *parasaccharone*, which crystallises from water in leaflets or prisms and melts at 159—160°. Parasaccharone is the lactone of parasaccharonic acid, the constitution of which is expressed either by

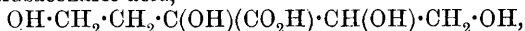


or by $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}(\text{OH})(\text{CO}_2\text{H}) \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2\text{H}$.

Calcium parasaccharonate, prepared by the addition of calcium

chloride to the potassium salt, separates in leaflets; the *copper* salt separates in needles.

When parasaccharic acid,



in the form of its barium salt, is oxidised by concentrated nitric acid, a syrup is obtained which, on neutralisation with sodium hydroxide and subsequent addition of calcium chloride, forms *calcium hydroxycitrate*, which separates from water in plates and crystallises with $18\text{H}_2\text{O}$. The free *acid*, $\text{C}_6\text{H}_8\text{O}_8 \cdot \text{H}_2\text{O}$, separates in needles or plates and melts at the same temperature as parasaccharone, namely, $159-160^\circ$. The *potassium* salt forms glistening pyramids and crystallises with $4\text{H}_2\text{O}$. The *copper* salt crystallises in pyramids. A. McK.

Ultramicroscopic Observations on Solutions of Pure Glycogen. Madame Z. GATIN-GRUŻEWSKA and WILHELM BILTZ (*Pflüger's Archiv*, 1904, 105, 115—120).—Solutions of pure glycogen (this vol., i, 295) have been examined by Raehlmann's method (*Berl. Med. Woch.*, 1904, 186) with a Siedentopf and Zsigmondy ultramicroscope. Raehlmann's results are confirmed, except in the case of extremely dilute solutions, where at most one or two particles could be observed in the field of vision at the same time.

Admixture with dilute saline solutions does not affect the general appearance, but the addition of precipitants, such as acetic acid or alcohol, does so. With acetic acid, a number of particles of the same size and of rapidly changing colour were observed in the field, and the light was found to be polarised. On the addition of absolute alcohol, numerous distinct particles were observed, the number of such increasing with the amount of alcohol, and most of these had a characteristic movement.

These phenomena point to the colloidal nature of glycogen solutions. J. J. S.

Hydrolytic Products of Sugar Cane Fibre. C. A. BROWNE, jun. (*J. Amer. Chem. Soc.*, 1904, 26, 1221—1235).—The reactions of thin sections of the sugar cane with various reagents are given. By the action of zinc chloride and iodine, no coloration is produced, showing that the cellulose is completely combined with other substances. After boiling with dilute sodium hydroxide, however, the blue coloration characteristic of cellulose is obtained without difficulty. A proximate analysis of the different tissues of the sugar cane has been made, and the results show that the degree of lignification is greatest in the rind and smallest in the pith.

The fibre of the sugar cane was digested with 5 per cent. solution of sodium hydroxide at 100° for 8 hours. On treating the liquid with 95 per cent. alcohol, a precipitate of cane gum was obtained, which, when dry, amounted to 25 per cent. of the original fibre. This substance dissolved sparingly in hot water, forming an opalescent solution, had $[\alpha]_D - 83.2^\circ$, and on distilling with hydrochloric acid yielded 44.88 per cent. of furfuraldehyde equivalent to 76.43 per cent. of pentosans; it contained 12 per cent. of inorganic matter.

When the gum was heated at 100° for 10 hours with 4 per cent. hydrochloric acid, xylose and arabinose were produced in proportions which indicate that xylan and araban constitute nearly 80 per cent. of the gum in the probable ratio of about five of the former to one of the latter.

The alkaline filtrate from the gum was evaporated until all the alcohol had been expelled, and was afterwards acidified with dilute sulphuric acid. A dark brown precipitate of lignin was obtained, which, when dry, amounted to 10.78 per cent. of the weight of the original fibre. The dry product formed a brown powder, soluble in water or alcohol; when heated with hydrochloric acid, it gave no trace of furfuraldehyde. The acid filtrate from the lignin precipitate contained a quantity of acetic acid corresponding with 5.23 per cent. of the original fibre.

The fibre, after being treated with sodium hydroxide, was washed with hot water and alcohol; it was then of a light straw colour, and amounted to about 42 per cent. of the original material. On distilling with hydrochloric acid, it yielded 5.07 per cent. of furfuraldehyde. When this fibre was hydrolysed with sulphuric acid, dextrose was produced.

E. G.

Alkylamines containing Fluorine. FRÉDÉRIC SWARTS (*Bull. Acad. Roy. Belg.*, 1904, 955—969. Compare this vol., i, 853).—When difluorobromoethane is heated with ammonia dissolved in alcohol at 160—170°, ethyl ether, difluoroethylamine, tetrafluorodiethylamine, and tetrafluorotriethylamine, $\text{NEt}(\text{CH}_2\cdot\text{CHF}_2)_2$, are formed.

The last of these may be separated from the associated secondary amine by converting this into the nitroso-derivative, distilling the mixture, and dissolving out the tertiary amine with hydrochloric acid and regenerating and purifying in the usual way. Tetrafluorotriethylamine is a colourless liquid with an odour recalling that of chloroacetal; it boils at 137° under 754 mm. pressure, and is almost insoluble in water. It is a very weak base, and aqueous solutions of its salts are acid to indicators; the *hydrochloride*, obtained by the action of hydrogen chloride on the amine dissolved in ether, is deliquescent. The amine decomposes at a red heat forming hydrogen fluoride and hydrogen cyanide. The electrical conductivity of the base could not be determined, but for the hydrochloride, $\mu_{1024}-\mu_{32}$ was approximately equal to 170. Tetrafluorotriethylamine is not produced by the action of ethyl alcohol on tetrafluorodiethylamine itself, but only in presence of haloid salts of this or of the primary amine, which seem to behave like zinc and stannic chlorides (compare Merz and Gasiorowski, *Abstr.*, 1884, 984). The etherification of the alcohol in the foregoing reaction is due to the action of the haloid salts of the amines, and experiments showed that the salts of tetrafluorodiethylamine were more active than those of difluoroethylamine in this respect, which appears to indicate that the etherification is really brought about by the acids liberated by the hydrolysis of the haloid salts of the amines. Reynoso observed (*J. pr. Chem.*, 1857, [i], 69, 52) that small quantities of ether were produced by heating hydrochlorides of morphine and cinchonine with alcohol at 200°.

T. A. H.

Action of Ammonia and Ethylamine on the Esters of Sulphonic Acids. WILHELM AUTENRIETH and RENÉ BERNHEIM (*Ber.*, 1904, 37, 3800—3809. Compare Carius, *J. pr. Chem.*, 1870, [ii], 2, 262).—Cold alcoholic ammonia reacts with the esters of both aliphatic and aromatic sulphonic acids yielding an alkylamine salt, $R \cdot SO_2 \cdot OR' + NH_3 = R \cdot SO_2 \cdot ONH_3R'$; a considerable amount, however, of the ammonium salt of the acid is formed at the same time. Sulphonamides are either not formed or formed only in minute quantities. The formation of the ammonium and alkylamine salts is probably due to the liberation of the free acid by the action of ammonia on the ester, $R \cdot SO_2 \cdot OEt + NH_3 = R \cdot SO_2 \cdot OH + NH_2Et$, and the free acid then combines with the excess of ammonia and the liberated amine according to the laws of mass action. With butyl benzene-sulphonate, no butylamine salt is formed.

The ethyl esters of ethanesulphonic acid, benzenesulphonic acid, ethane- $\alpha\beta$ -disulphonic acid, ethane- $\alpha\alpha$ -disulphonic acid, and of propane- $\alpha\gamma$ -disulphonic acid have been treated in this way, also methyl benzene-sulphonate. Concentrated aqueous ammonia may be used in place of the alcoholic with similar results.

Ethyl benzenesulphonate and ethylamine yield a small amount of *diethylamine benzenesulphonate* melting at 139° . Ethyl ethanesulphonate and ethyl benzenesulphonate with aniline gave small amounts of the corresponding *aniline* salts melting respectively at 142° and 234° . The formation of these was probably due to the presence of a small amount of free acid in the esters.

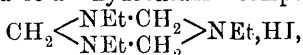
Ethyl ethane- $\alpha\beta$ -disulphonate crystallises in long prisms and melts at 77.5° .

Most of the salts were obtained by the addition of ether and are hygroscopic. The presence of ethylamine was detected by conversion into benzenesulphonethylamide (m. p. 58°). J. J. S.

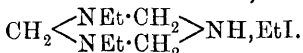
Abnormal Salt-formation in the Case of the Trialkyltrimethylenetriamines. ALFRED EINHORN and AUGUST PRETTNER (*Annalen*, 1904, 334, 210—233. Compare Abstr., 1902, i, 840).—It has been shown (*loc. cit.*) that the hydriodide of triethyltrimethylenetriamine, $CH_2 \begin{smallmatrix} \text{NEt} \cdot \text{CH}_2 \\ \text{NEt} \cdot \text{CH}_2 \end{smallmatrix} \text{NEt}$, is converted to the extent of 10 per cent., when heated, into an isomeric hydriodide, which behaves as a quaternary ammonium salt. Both compounds can also be obtained from the methiodide of triethyltrimethylenetriamine, the normal salt being produced when the alcoholic solution is allowed to evaporate at a low temperature, and the quaternary salt when the alcoholic solution is boiled before evaporation. Towards alkali carbonates and hydroxides, these salts behave differently; from the normal salt, the base is completely displaced, whilst the quaternary salt is unchanged by potassium carbonate and by potassium hydroxide at a low temperature, but at a higher temperature is decomposed, yielding a mixture of triethyltrimethylenetriamine and an ammonium base. The same base, which could not be isolated, is also obtained by using silver oxide; its solution can be reconverted into the iodide. Two series of picrates and bromides exist. From the fact that the abnormal iodide

can be directly converted into the picrate, a behaviour characteristic of quaternary salts, whilst the normal salt is merely decomposed by picric acid, it is concluded that the abnormal salt is a quaternary compound. All the quaternary salts are able to form additive compounds with iodoform, whilst the normal salts are not.

After discussion, it is suggested that this isomerism is best accounted for on Werner's hypothesis (Abstr., 1902, ii, 554), according to which the normal salt would be a "hydronium" compound,



and the abnormal salt a "carbonium" salt,



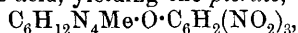
Triethyltrimethylenetriamine (b. p. 196—198°) is prepared by adding an ice-cold solution of ethylamine to a 40 per cent. solution of formaldehyde. The normal *hydriodide* (m. p. 121°) has a faint alkaline reaction, is decomposed by prolonged boiling of its aqueous solution, and immediately on addition of picric acid or dilute hydrochloric acid, an oil being formed; platonic chloride also decomposes the salt, with the production of ethylamine platinichloride. The hydrobromide crystallises in needles melting and decomposing at 123°. The *picrate*, $(\text{CH}_2 \cdot \text{NEt})_3 \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{OH}$, prepared by bringing together the components in ethereal solution, crystallises in pale yellow needles and sinters and melts at 65°; the *dipicrate* is prepared in a similar manner. The *methiodide*, $(\text{CH}_2 \cdot \text{NEt})_3 \cdot \text{MeI}$, formed by adding methyl iodide to an ethereal solution of the base, is a hygroscopic, white powder melting at 98—99°.

The abnormal *hydriodide*, prepared as previously described, crystallises in three-cornered leaflets melting at 199—200°, is neutral in aqueous solution, and is stable on heating. The *additive* compound with iodoform, $\text{C}_3\text{H}_6\text{Et}_3\text{N}_3 \cdot \text{HI} \cdot \text{CHI}_3$, formed on bringing the components together in methyl alcoholic solution, crystallises in needles melting at 133—134°. The *hydrobromide* is prepared by shaking a solution of the iodide with silver bromide and crystallises in hexagonal plates melting at 182°; the *platinichloride* crystallises in rhombic needles decomposing at 215°; the *picrate*, readily prepared directly from the hydriodide, crystallises in yellow needles melting at 108°.

Trimethyltrimethylenetriamine yields also two series of salts. The *methiodide* of the base is prepared by bringing the components together in ethereal solution, and is very hygroscopic. The normal *hydriodide* melts and decomposes at 116°, and when heated at 116—135° is converted into a salt melting at 150—152°, which is not homogeneous, but a mixture of an isomeric hydriodide with trimethylamine hydriodide; a similar mixture is obtained when the alcoholic solution of the methiodide is boiled. The salts can be separated by converting the quaternary ammonium compound into the additive compound with iodoform, which is more soluble than the corresponding *additive* compound with trimethylamine, $\text{NMe}_3 \cdot \text{HI} \cdot \text{CHI}_3$; the latter crystallises in pale yellow needles melting at 200°; the *additive* compound of the ammonium base, $\text{C}_6\text{H}_3\text{Me}_3\text{N}_3 \cdot \text{HI} \cdot \text{CHI}_3$, crystallises in needles melting at 125°. The abnormal *hydriodide* prepared from the iodoform

additive compound crystallises in six-sided plates melting at 166° , and can be obtained unchanged from its aqueous solution. The corresponding *picrate*, prepared from the hydriodide, melts at 159 — 160° .

The *methiodide* of hexamethylenetetramine, $C_6H_{12}N_4 \cdot MeI$, prepared by prolonged heating of methyl iodide and hexamethylenetetramine iodide in alcoholic solution, crystallises in needles melting at 204° , and reacts with picric acid, yielding the *picrate*,



which crystallises in yellow needles melting at 215° . K. J. P. O.

Triaminoguanidine. ROBERT STOLLÉ (*Ber.*, 1904, 37, 3548—3549).—*Triaminoguanidine hydrochloride*, $NH_2 \cdot N : C(NH \cdot NH_2)_2 \cdot HCl$, formed when hydrazine hydrate is boiled with an excess of carbon tetrachloride in a current of ammonia in a reflux apparatus for some days, crystallises from alcohol in slender needles and melts and decomposes at 228° . The *tribenzylidene* derivative, obtained, along with benzylideneazine, by shaking the aqueous solution of the crude hydrochloride with benzaldehyde, crystallises in yellow, microscopic needles, melts at 196° , and, when boiled with dilute hydrochloric acid, yields benzaldehyde, *s*-diaminocarbamide, and a condensation *product* which melts at about 240° . G. Y.

Esters of Nitrocentricarboxylic Acid and Similar Compounds. OTTO DIELS and PAUL NAWIASKY (*Ber.*, 1904, 37, 3672—3683. Compare *Abstr.*, 1903, i, 324).—*Methyl ethyl iminodicarboxylate*, $CO_2Me \cdot NH \cdot CO_2Et$, obtained by the action of methyl chlorocarbonate on the sodium derivative of urethane, crystallises from a mixture of ether and light petroleum in glistening needles melting at 73° after sintering at 68° . It dissolves readily in most solvents, and with concentrated potassium hydroxide yields a precipitate of the *potassium* derivative. The same ester is formed by the action of ethyl chlorocarbonate on the sodium derivative of methyl carbamate.

Dimethyl ethyl nitrocentricarboxylate, $CO_2Et \cdot N(CO_2Me)_2$, obtained by the action of methyl chlorocarbonate on the disodio-derivative of urethane, is a colourless liquid, distilling at 131° under 8 mm. or at 144 — 145° under 12.5 mm. pressure. It has n_D 1.43386 and the sp. gr. 1.2146 at 22° . When hydrolysed with cold potassium hydroxide, the ester yields methyl ethyl iminodicarboxylate, carbon dioxide, and methyl alcohol. With cold 25 per cent. ammonia, it yields methyl and ethyl allophanates, cyanuric acid, and methyl and ethyl carbamates.

Ethyl diamyl nitrocentricarboxylate, obtained by the action of amyl chlorocarbonate on disodiourethane, is a clear oil distilling at 184 — 186° under 13 mm. pressure, has a sp. gr. 1.0380 at 15° , and is strongly refractive.

Dicarbethoxyglycine ester (ethyl dicarbethoxyaminoacetate),
 $N(CO_2Et)_2 \cdot CH_2 \cdot CO_2Et$,

obtained by the action of ethyl chlorocarbonate on carbethoxyglycine ester, crystallises from light petroleum in stout prisms melting at 36.5° and boiling at 152 — 153° under 10 mm. pressure. With ammonia, at 20 — 30° , it yields carbethoxyglycinamide.

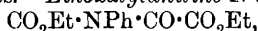
Ethyl dicarbethoxy-oxamate, $\text{N}(\text{CO}_2\text{Et})_2 \cdot \text{CO} \cdot \text{CO}_2\text{Et}$, obtained by the action of ethyl oxalyl chloride, $\text{COCl} \cdot \text{CO}_2\text{Et}$ (boiling at $133\text{--}135^\circ$), on the potassium derivative of ethyl iminodicarboxylate, is a colourless oil, which distils at $170\cdot5\text{--}171\cdot5^\circ$ under 11 mm. pressure, does not solidify in a freezing mixture, and has a sp. gr. 1.1752 at 17° .

Ethyl iminodioxalate, $\text{NH}(\text{CO} \cdot \text{CO}_2\text{Et})_2$, obtained from ethyl sodiocarbamate and ethyl oxalylchloride, melts at $71\text{--}72^\circ$.

Ethyl diethoxalylcarbamate, $\text{CO}_2\text{Et} \cdot \text{N}(\text{CO} \cdot \text{CO}_2\text{Et})_2$, is obtained, together with the ethyl carbethoxycarbamate (m. p. 47°), from disodiourethane and ethyl oxalylchloride. It is a colourless oil, distilling at $182\text{--}184^\circ$ under 9–10 mm. pressure, has a sp. gr. 1.2294 at 16° , and on hydrolysis in the cold yields potassium oxalate.

Ethyl aniline-N-dicarboxylate, $\text{NPh}(\text{CO}_2\text{Et})_2$, obtained by the action of ethyl carbonate on sodiophenylurethane, crystallises from acetone and light petroleum in large prisms, which sinter at 58° and melt at 62° . It dissolves readily in most solvents, is stable towards alkalis, and with ammonia yields phenyl urethane.

Methyl ethyl aniline-N-dicarboxylate, $\text{CO}_2\text{Me} \cdot \text{NPh} \cdot \text{CO}_2\text{Et}$, obtained by using methyl chlorocarbonate, sinters at 65° , melts at 69° , is only sparingly soluble in ether, and is very sparingly soluble in water, light petroleum, or concentrated hydrochloric acid. *Methyl aniline-N-dicarboxylate*, $\text{NPh}(\text{CO}_2\text{Me})_2$, melts at $142\text{--}143^\circ$ and crystallises from ether in quadratic plates. *Ethoxalylaniline-N-carboxylate*,



sinters at 64° , melts at 68° , and distils at $188\text{--}190^\circ$ under 8–9 mm. pressure. J. J. S.

Alkylated Aminoacetonitriles. EMIL KNOEVENAGEL and ERNST MERCKLIN (*Ber.*, 1904, 37, 4087–4094. Compare this vol., i, 989).—*Sodium diethylaminomethanesulphonate*, $\text{NEt}_2 \cdot \text{CH}_2 \cdot \text{SO}_3\text{Na}$, formed by the action of diethylamine on formaldehyde and sodium hydrogen sulphite in aqueous solution, separates from alcohol in crystals, when heated on platinum, swells up, burns, melts, and leaves a carbonaceous residue, and yields tetraethylmethylenediamine when heated with dilute hydrochloric acid, with aqueous potassium hydroxide, or with phosphorus pentachloride and alcohol successively. *Acetyldiethylaminomethanol*, $\text{NEt}_2 \cdot \text{CH}_2 \cdot \text{OAc}$, formed when sodium diethylaminomethanesulphonate is boiled with acetic anhydride, boils at $81\text{--}82^\circ$ under 14.5 mm. pressure. Diethylaminoacetonitrile, formed by the action of potassium cyanide on the sodium sulphonate, boils at $62\cdot5^\circ$ under 14 mm. pressure; the methiodide melts at 186° , the hydrochloride crystallises in small, white needles and melts at 186° (Klages and Margolinsky, this vol., i, 146).

α -Diethylaminopropionitrile is formed by the action of aqueous potassium cyanide on the additive compound of diethylamine, acetaldehyde, and sodium hydrogen sulphite (Klages and Margolinsky, *loc. cit.*). α -Diethylaminoisohexonitrile, obtained similarly from isovaleraldehyde, boils at $88\cdot5\text{--}89^\circ$ under 11 mm. pressure; α -diethylamino-n-octonitrile, $\text{NEt}_2 \cdot \text{CH}(\text{C}_6\text{H}_{13}) \cdot \text{CN}$, obtained from heptaldehyde, boils at $125\text{--}126^\circ$ under 11 mm. pressure; α -diethylaminobenzyl cyanide, formed from

benzaldehyde, boils at 130—131° under 11 mm. pressure (Klages and Margolinsky, *loc. cit.*); *α*-diethylamino-*p*-methoxybenzyl cyanide, obtained from anisaldehyde, crystallises in white needles, melts at 44°, boils at 166° under 11 mm. pressure, and is hydrolysed by concentrated sulphuric acid and aqueous alcoholic sodium hydroxide to *α*-diethylamino-*p*-methoxyphenylacetamide, which crystallises in small, white needles and melts at 161°. The *methylene ether* of diethylamino-3:4-dihydroxyphenylacetonitrile, obtained from piperonal, melts at 43—44° and boils at 179.5° under 12.5 mm. pressure.

Ethylaminoacetonitrile, $\text{NHEt}\cdot\text{CH}_2\cdot\text{CN}$, boils at 81—83° under 29 mm., or at 166—167° under atmospheric pressure; with phenylcarbimide, it forms the *phenylcarbamide*, $\text{NHPh}\cdot\text{CO}\cdot\text{NEt}\cdot\text{CH}_2\cdot\text{CN}$, which sinters at 107° and melts at 116°. The *phenylthiocarbamide*, $\text{C}_{11}\text{H}_{13}\text{N}_2\text{S}$, crystallises in yellow needles and melts at 184—185°.

Ethyliminobisacetonitrile, $\text{NEt}(\text{CH}_2\cdot\text{CN})_2$, is a colourless oil and boils at 141° under 13 mm. pressure; the *hydrochloride*, $\text{C}_6\text{H}_{10}\text{N}_3\text{Cl}$, crystallises in white needles and melts at 110—112°.

α-Ethylaminoisohexonitrile, $\text{NHEt}\cdot\text{CH}(\text{C}_4\text{H}_9)\cdot\text{CN}$, obtained from *iso*-valeraldehyde, boils at 83.5—84° under 12 mm. pressure; *α*-ethylamino-*n*-octonitrile, $\text{NHEt}\cdot\text{CH}(\text{C}_6\text{H}_{13})\cdot\text{CN}$, boils at 122° under 12 mm. pressure. G. Y.

Derivatives of Glycollonitrile. LOUIS HENRY (*Bull. Acad. Roy. Belg.*, 1904, 895—906. Compare *Abstr.*, 1890, i, 739; 1899, i, 182, 183, 255, and 567).—When chloroacetonitrile is warmed with dry potassium formate, *cyanomethyl formate*, $\text{H}\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CN}$, is produced. This is a colourless liquid with a slight odour; it boils at 172—173° under 759 mm. pressure, has a sp. gr. 1.182 at 20° and n_D^{20} 1.40918 at 20°, and is hydrolysed by water into glycollonitrile and formic acid; with methyl alcohol, the latter is eliminated as methyl formate. *Cyanomethyl acetate*, $\text{CN}\cdot\text{CH}_2\cdot\text{OAc}$, similarly prepared, boils at 179—180° under 75 mm. pressure, has a sp. gr. 1.105 at 20° and n_D^{20} 1.4107 at 20°. It is only slowly hydrolysed by boiling water, forming glycollonitrile as one product.

Cyanomethyl propionate is a colourless liquid possessing a slight odour. It boils at 188—189° under 759 mm. pressure, has a sp. gr. 1.062 at 20° and n_D^{20} 1.41662 at 20°. *Cyanomethyl n-butyrate* is a liquid with a faint butyric odour; it boils at 200° under 758 mm. pressure and has n_D^{20} 1.42131 at 20°. Comparison of the boiling points of these cyano-derivatives with those of the ethyl esters of the same acids show that the value of the increase in boiling point due to the replacement of a CH_3 -group by the CN -group decreases as the series is ascended. Chloroacetonitrile reacts readily with ammonia and with primary and secondary amines, but the cyanoamines of the type $\text{CN}\cdot\text{CH}_2\cdot\text{NX}_2$ so formed are more readily obtained by the interaction of glycollonitrile with the secondary amines. Comparing these cyanoamines with the corresponding ethylamines, it is seen that here also the replacement of $-\text{CH}_3$ by $\text{CN}-$ results in an elevation of the boiling point, and the value of this increment decreases as the series is ascended.

T. A. H.

Double Cyanides of Mercury. HERMANN GROSSMANN and PETER VON DER FORST (*Ber.*, 1904, 37, 4141—4144).—The *potassium* salt has the composition $K_2Hg(CN)_4$, and the *sodium* salt $NaHg(CN)_3$, but conductivity measurements show the presence of double molecules, $Na_2Hg_2(CN)_6$. The *barium* and *strontium* compounds crystallise in needles, their composition being $BaHg(CN)_4 \cdot 3H_2O$ and $SrHg(CN)_4 \cdot 5H_2O$ respectively. The *calcium* salt, $CaHg_2(CN)_6 \cdot 3H_2O$, crystallises in colourless, very hygroscopic needles, whilst $Ca_2Hg_3(CN)_{10} \cdot 6H_2O$ forms four-sided platelets. The *magnesium* salt has the composition $Mg_2Hg_3(CN)_{10} \cdot 5H_2O$.
E. F. A.

New Method of preparing Organic Derivatives of Phosphorus. VICTOR AUGER (*Compt. rend.*, 1904, 139, 639—641).—By the action of methyl iodide on a solution of phosphorus in alcoholic sodium hydroxide containing water (compare Michaelis and Pitsch, *Abstr.*, 1900, ii, 137; 1903, ii, 207), a mixture of primary, secondary, and tertiary phosphines are obtained and isolated after oxidation as methylphosphinic acid, dimethylphosphinic acid, and trimethylphosphine oxide respectively; when *isoamyl* iodide replaces methyl iodide in the above reaction, the principal products are *isoamyl*phosphinic acid and *diisoamyl*phosphinic acid.

Attempts to prepare normal sodium phosphite, Na_3PO_3 , by the action of excess of sodium ethoxide on an alcoholic solution of phosphorous acid were unsuccessful, disodium hydrogen phosphite, Na_2HPO_3 , being the only product; the author therefore concludes that Zimmermann's normal sodium phosphite does not exist (compare *Abstr.*, 1874, 655).
M. A. W.

Action of the Halogen Derivatives of Tervalent and Quinquevalent Metalloids on Alkyl Haloids. VICTOR AUGER (*Compt. rend.*, 1904, 139, 671—672. Compare preceding abstract).—A mixture of the periodides of the mono-, di-, and tri-alkyl-phosphines, of which two-thirds is the di-substituted compound, is obtained by the action of phosphorus di-iodide and methyl, ethyl, or propyl iodide in the proportion of $3RI$ to P_2I_4 at 180 — 210° , and a similar reaction is obtained when phosphorus tribromide or trichloride replaces the phosphorus di-iodide. Arsenic chloride does not react with ethyl or methyl iodide even at 210° ; antimony chloride and ethyl iodide at 150 — 160° give antimony iodide and ethyl chloride, together with a small quantity of an ethyl derivative of antimony which has not yet been separated; bismuth chloride and ethyl iodide give only bismuth iodide and ethyl chloride.
M. A. W.

Action of Organomagnesium Solutions on the Halogen Derivatives of Phosphorus, Arsenic, or Antimony. VICTOR AUGER and M. BILLY (*Compt. rend.*, 1904, 139, 597—599. Compare this vol., i, 22, 724).—Magnesium methyl iodide reacts with phosphorus di-iodide at the ordinary temperature to form tetramethylphosphonium iodide, and with phosphorus trichloride at -20° to form tetramethylphosphonium chloride and phosphorus di-iodide; if, how-

ever, the crude product is treated with nitric acid and sodium nitrite, red crystals of *tetramethylphosphonium periodide*, $\text{PMe}_4\text{I} \cdot \text{I}_2$, are obtained. Magnesium methyl bromide at -30° gives, with phosphorus trichloride, a mixture of mono-, di-, and tri-alkyl substituted derivatives of phosphine, which, on oxidation, yield monomethylphosphinic acid, dimethylphosphinic acid, and trimethylphosphine oxide respectively, the yield of the disubstituted derivative being equal to the sum of the other two.

Magnesium ethyl bromide reacts at low temperatures with arsenic trichloride, and the product, after oxidation, consists principally of triethylarsine oxide, together with small quantities of monomethylarsonic acid and diethylarsonic acid.

Ethylstibine iodide, SbEtI_3 , crystallising in golden-yellow scales melting at 43° and decomposing at 200° , is isolated by the action of potassium iodide on the mixed product obtained from the action of magnesium ethyl bromide on antimony trichloride at -18° .

M. A. W.

Amphoteric Nature of Cacodylic Acid. JOHN JOHNSTON (*Ber.*, 1904, 37, 3625—3627. Compare Zawidzki, *Abstr.*, 1903, i, 801; this vol., i, 232, 564; Hantzsch, this vol., i, 725).—In the determinations of the electrical conductivity of aqueous solutions of cacodylic acid made by Zawidzki, the water used by him was not sufficiently pure to permit of his results at large dilutions being of theoretical importance. The author has measured the conductivity of aqueous solutions of cacodylic acid at 25° , using water with $K = 0.65 \times 10^{-6}$ at 18° . From the figures quoted, the Ostwald "constant" increases very considerably, and this points to the amphoteric nature of the acid. The acid constant, k_a , is taken as 6.4×10^{-7} , the ratio k_b/K as 32, μ_∞ (acid) as 354.5, and μ_∞ (salt) as 61. The experimental values are in accordance with the theory advanced by Walker (this vol., ii, 509).

A. McK.

Nitration of *o*-Dichlorobenzene. RUDOLF NIETZKI and ADOLF KONWALDT (*Ber.*, 1904, 37, 3892—3893).—*o*-Dichlorobenzene yields two dinitro-derivatives on nitration, which may be separated by fractional crystallisation.

1:2-Dichloro-4:5-dinitrobenzene melts at 114° and yields the dichloronitroaniline melting at 175° when heated with alcoholic ammonia. One nitro-group is removed by heating with aniline hydrochloride.

1:2-Dichloro-3:4-dinitrobenzene melts at 53 – 55° and loses both atoms of chlorine when heated with ammonia, the nitro-groups remaining intact (compare Hartley and Cohen, *Trans.*, 1904, 85, 867).

C. H. D.

Magnesium Amalgam as a Reducing Agent. THOMAS EVANS and WILLIAM C. FETSCH (*J. Amer. Chem. Soc.*, 1904, 26, 1158—1161).—Magnesium amalgam containing 5 or 10 per cent. of magnesium may be readily prepared by triturating mercury with powdered magnesium, the latter being added in small quantities at a time. The amalgam decomposes water rapidly with evolution of hydrogen, but is without action on cold, dry alcohol, and is therefore a convenient

reagent for the preparation and preservation of absolute alcohol. When alcohol is boiled for a long time with the amalgam, hydrogen is liberated and a pale yellow solution is obtained which, on evaporation and ignition, yields a very small residue of magnesium oxide.

When a strong alcoholic solution of nitrobenzene is treated with magnesium amalgam in slight excess of the quantity theoretically required to reduce it to phenylhydroxylamine, hydrogen is evolved and azobenzene is obtained in a yield amounting to 95.66 of the theoretical. No hydrazobenzene is produced in this reaction.

E. G.

Reducing Action of Magnesium Amalgam on Aromatic Nitro-compounds. THOMAS EVANS and HARRY S. FRY (*J. Amer. Chem. Soc.*, 1904, 26, 1161—1171).—When a dilute solution of nitrobenzene in 93 per cent. ethyl alcohol is treated with the quantity of magnesium amalgam theoretically required to convert it into aniline and, after the whole of the amalgam has been decomposed, the solution is heated for 15 hours under a reflux condenser, azoxybenzene is produced, the yield amounting to 89.9 per cent. of the theoretical. If methyl alcohol is used instead of ethyl alcohol, an 88.5 per cent. yield of azobenzene is obtained.

When *m*-dinitrobenzene is similarly treated with magnesium amalgam in presence of ethyl alcohol, *m*-dinitroazoxybenzene is produced, the yield amounting to 70 per cent. of the theoretical. If methyl alcohol is employed, the same product is obtained, but the yield is only 54.37 per cent.

o-Nitrotoluene is reduced by magnesium amalgam in presence of ethyl alcohol with formation of a 50 per cent. yield of *o*-azoxytoluene, whilst in presence of methyl alcohol a 66.5 per cent. yield of *o*-azotoluene is obtained.

p-Nitrotoluene in solution in ethyl alcohol gives a 90 per cent. yield of *p*-azoxytoluene, whilst with methyl alcohol the product consists of 22.2 per cent. of the theoretical yield of *p*-azoxytoluene, 23.9 per cent. of that of *p*-azotoluene, and 38 per cent. of unchanged *p*-nitrotoluene.

These results show that when a dilute solution of a nitro-compound in ethyl alcohol is reduced with magnesium amalgam, an azoxy-derivative is formed, whilst in methyl alcohol solutions there is a tendency for the azo-derivative to be produced. The following experiments were undertaken with a view to ascertain the cause of this difference in the behaviour of the two alcohols.

When pure dry methyl alcohol is heated with magnesium amalgam, magnesium methoxide is produced, which gradually separates from the cold solution in long, prismatic crystals. If ethyl alcohol is heated with the amalgam, magnesium ethoxide is formed as an insoluble precipitate. It is probable, therefore, that the reason that the reduction proceeds further in dilute methyl alcohol than in dilute ethyl alcohol solution is that the magnesium methoxide is soluble, and is therefore readily oxidised to the formate, whilst the ethoxide, being insoluble, has a much weaker reducing action. In order to obtain confirmation of the reducing action of the methoxide, a solution of

nitrobenzene in methyl alcohol was treated with magnesium amalgam without the application of heat. In this case, azoxybenzene was formed as the chief product of the reduction, together with a smaller quantity of azobenzene. It is evident, therefore, that the azoxybenzene is formed first, and is subsequently reduced to azobenzene when boiled with a solution of magnesium methoxide.

It has been shown by Evans and Fetsch (preceding abstract) that when a strong solution of nitrobenzene in ethyl alcohol is reduced by magnesium amalgam, azobenzene is the chief product of the reaction. When a concentrated solution of *p*-nitrotoluene in 95 per cent. ethyl alcohol is similarly treated, a mixture of *p*-azotoluene and *p*-azoxytoluene is produced. It is probable that the greater reducing action of the amalgam in the hot concentrated solution is due to part of the magnesium ethoxide undergoing oxidation as it is formed. When, however, the reduction is carried out in a cold solution, the ethoxide is precipitated and consequently takes no further part in the reaction.

E. G.

Influence of the Cathode Material on the Reduction of *m*- and *p*-Nitrotoluenes. WALTHER LÖB and JOS. SCHMITT (*Zeit. Elektrochem.*, 1904, 10, 756—764).—The nitro-compounds are suspended in 2 per cent. sodium hydroxide solution contained in a porous pot; cathodes of nickel, zinc, and of copper with and without copper dust are used. The products in every case were the azoxytoluene, hydrazotoluene, and toluidine. When *p*-nitrotoluene is used, some *p*-azotoluene is also formed. The most feeble reduction is observed with nickel; zinc, copper, and copper + copper dust giving more energetic reduction in the order mentioned. Not only is the current efficiency better with the last-named cathode, but the reduction goes further, toluidine being the predominant product with copper, whilst azoxytoluene is the main product with nickel. *p*-Nitrotoluene is more easily reduced than *m*-nitrotoluene. The electrolytic reduction of *m*-nitrotoluene with a nickel cathode might be employed as a method of preparation of *m*-azoxytoluene, and the toluidines might be suitably prepared by reduction with a copper cathode in presence of copper dust, but the other reductions studied lead to mixtures of substances which are only separated from each other with great difficulty.

T. E.

Tetrahydro- and Decahydro-naphthalenes. HENRI LEROUX (*Compt. rend.*, 1904, 139, 672—674).—Tetrahydronaphthalene, $C_{10}H_{12}$, obtained by the direct hydrogenation of naphthalene at 180° by Sabatier and Senderens' method (compare Abstr., 1901, i, 459), is a colourless liquid boiling at 206° (corr.), has a sp. gr. 0.984 at 0° or 0.966 at 20° , and n_D 1.5402 at 20° , and yields, on oxidation with potassium permanganate, *o*-carboxyhydrocinnamic acid. *Chlorotetrahydronaphthalene*, $C_{10}H_{11}Cl$, obtained by the direct action of chlorine on tetrahydronaphthalene, boils at 121 — 124° under 15 mm., or at 230° under atmospheric pressure, evolving hydrogen chloride. *Bromotetrahydronaphthalene*, $C_{10}H_{11}Br$, obtained by the action of bromine on the hydrocarbon, boils at 145 — 147° under 21 mm. and distills and decomposes at 250° under atmospheric pressure. Tetrahydronaphtha-

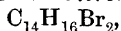
lene bromohydrin, $C_{10}H_{10}Br\cdot OH$, formed, together with the preceding compound, by the action of bromine on tetrahydronaphthalene, crystallises from acetone in magnificent prisms melting at 112° (corr.), and may be identical with the bromohydrin obtained by Bamberger and Lodter (compare Abstr., 1893, i, 591) by the action of hydrogen bromide on tetrahydronaphthylene oxide. *Decahydronaphthalene*, $C_{10}H_{18}$, obtained by hydrogenating tetrahydronaphthalene at 175° , is a colourless liquid with an odour of menthol, boils at 187 — 188° (corr.), has a sp. gr. 0.893 at 0° or 0.877 at 20° , and n_D 1.4675 at 20° , and differs in its physical properties from the compound of the same composition described by Wreden and Znatowick (compare Abstr., 1877, 899); it reacts readily with chlorine forming *chlorodecahydronaphthalene*, $C_{10}H_{17}Cl$, boiling at 112 — 115° under 18 mm. pressure, and *dichlorodecahydronaphthalene*, $C_{10}H_{16}Cl_2$, boiling at 145 — 148° under 18 mm. pressure.
M. A. W.

Terpenes and Ethereal Oils. LXVIII. Nitrites of some Cyclic Hydrocarbons. OTTO WALLACH [with ERICH BESCHKE] (*Annalen*, 1904, 336, 1—8. Compare this vol., i, 753).—Indene nitrite, obtained in the same manner as anethole nitrite (*loc. cit.*), yields β -nitroindene, which melts at 141° , when distilled in small quantities in a current of steam (Dennstedt and Ahrens, Abstr., 1895, i, 475). β -Hydrindone is obtained when β -nitroindene is reduced with zinc dust and acetic acid and the product hydrolysed with dilute sulphuric acid; the *semicarbazone*, $C_{10}H_{11}ON_3$, melts at 203 — 205° .

3-Methylindene nitrosochloride is a white, crystalline powder. *2-Nitro-3-methylindene*, $C_{10}H_9O_2N$, obtained along with an acid substance by the action of steam on 3-methylindene nitrosochloride, or by treatment of 3-methylindene with sodium nitrite in alcoholic acetic acid solution, forms large, yellow crystals, melts at 107 — 108° , and, when reduced with zinc and acetic acid, yields 3-methyl-2-hydrindone, which melts at 62 — 63° . The *semicarbazone* melts at 195° .
G. Y.

Tetrahydro- and Octahydro-anthracenes. MARCEL GODCHOT (*Compt. rend.*, 1904, 139, 604—606).—*Tetrahydroanthracene*, $C_{14}H_{14}$, obtained by the hydrogenation of anthracene by the method of Sabatier and Senderens (compare Abstr., 1900, i, 469, 470, 471; 1901, i, 195) at a temperature of 250° , forms colourless crystals melting at 89° and boiling at 309 — 313° , is insoluble in water, slightly soluble in warm alcohol or acetic acid, more readily so in boiling benzene, the solutions exhibiting a strong blue fluorescence; it yields anthraquinone on oxidation and 9:10-dichloro- and 9:10-dibromo-anthracenes on treatment with chlorine or bromine.

Octahydroanthracene, $C_{14}H_{18}$, prepared by the direct hydrogenation of anthracene at 200° , of anthraquinone at 250° , or of tetrahydroanthracene at 190° , crystallises in colourless plates melting and subliming at 71° and boiling at 292 — 295° , is insoluble in water, and soluble in warm alcohol, acetic acid, or benzene and its homologues, the solutions possessing a characteristic green fluorescence. The *picrate*, $2C_{14}H_{18}\cdot C_6H_3O_7N_3$, melts at 80° . *Dibromo-octahydroanthracene*,



crystallises in large, colourless needles melting at 194° (corr.), and is soluble in hot ethyl acetate, benzene, or chloroform, less readily so in alcohol or acetic acid, and the solutions are not fluorescent. *Dibromohexahydroanthracene*, $C_{14}H_{14}Br_2$, crystallises in thin, yellow needles melting at 162° (corr.) and exhibits a fine blue fluorescence in solution. *Bromo-octohydroanthracene*, $C_{14}H_{17}Br$, is a yellow liquid, readily soluble in the ordinary solvents, and loses HBr on distillation, forming a hydrocarbon not yet described. *Dichloro-octohydroanthracene*,
 $C_{14}H_{16}Cl_2$,

melts at 192° (corr.), *dichlorohexahydroanthracene* melts at 159° (corr.), *chloro-octohydroanthracene*, $C_{14}H_{17}Cl$, is a liquid. M. A. W.

Formation of Phenanthrene from Fluorene. CARL GRAEBE (*Ber.*, 1904, 37, 4145—4146).—On passing either ethyl- or methylfluorene through a glass tube heated to a faint red glow, phenanthrene is formed in considerable quantity. When 9-ethylfluorene is heated with lead oxide, reaction sets in at about 300° , and a hydrocarbon is formed, melting at 99 — 100° , and yielding a characteristic *picrate*, which melts at 156° . This is perhaps 9-methylphenanthrene.

E. F. A.

Triphenylmethyl. X. MOSES GOMBERG and L. H. CONE (*Ber.*, 1904, 37, 3538—3547. Compare *Abstr.*, 1901, i, 77, 319, 638, 690; 1902, i, 534, 600, 754; 1903, i, 81, 244; this vol., i, 658).—The formation of triphenylmethyl peroxide by the action of oxygen on triphenylmethyl is accompanied by a development of heat. The yield of peroxide is 63—69.5 per cent. of the theoretical, or 80.3—86.6 if air is used instead of oxygen; about 20 per cent. of the peroxide formed decomposes immediately to oily products which are soluble in ether and contain about the same amount of oxygen as the peroxide.

Triphenylmethyl sulphate, $(CPh_3)_2SO_4$, formed by the action of silver sulphate on triphenylmethyl chloride, is dark red, forms intensely red solutions, has the conductivity $\mu_{10} = 49$ when dissolved in liquid sulphur dioxide, and is hydrolysed by moisture to triphenylcarbinol and sulphuric acid.

The action of bromine on triphenylmethyl peroxide in chloroform solution leads to the formation of *triphenylbromomethane pentabromide*, $C_{19}H_{15}Br_5$, which is an unstable, dark red, crystalline substance. In carbon tetrachloride solution, the action of bromine on the peroxide leads to the formation of triphenylmethyl bromide. Triphenylbromomethane pentaiodide is formed by the action of bromine and an excess of iodine on the peroxide in chloroform solution. In boiling carbon tetrachloride solution in presence of iodine, the peroxide reacts with chlorine to form triphenylmethyl chloride, benzophenone chloride, and a substance which melts at 66 — 67° and is probably 2:4'-dichlorobenzophenone. The action of phosphorus pentachloride on the peroxide leads to the formation of benzophenone chloride and phenyldiphenylenemethane, which melts at 144° .

Whilst triphenylmethyl solutions undergo only slight decomposition when exposed to diffuse light, even after a year, a 15 per cent. solution in benzene is completely decolorised by exposure to direct sun-

light for 3—4 hours; the reaction takes place more rapidly in carbon tetrachloride, more slowly in carbon disulphide solution. The distillation residue from the benzene solution consists of triphenylmethane (65 per cent.), products insoluble in ether (25 per cent.), and an oil with a strong aromatic odour. The products insoluble in ether are an unsaturated substance which melts at about 237° and a saturated substance which melts at 194° . The distillation residue from the carbon tetrachloride solution consists of 50 per cent. of an oil and a mixture of crystalline substances, but no triphenylmethane.

The analogues of triphenylmethyl are still more sensitive to light.

G. Y.

The Triboluminescent Parent Hydrocarbon of Rosaniline. AUGUSTIN BISTRZYCKI and JOSEPH GYR (*Ber.*, 1904, **37**, 3696—3699. Compare this vol., i, 498, and E. and O. Fischer, *ibid.*, 863).—Careful comparisons of the hydrocarbons obtained by the authors, by E. and O. Fischer, and by Hemilian have established their identity. The latter gives a yellow coloration when rubbed with concentrated sulphuric acid, but this is probably due to a small amount of impurity. All three specimens exhibit triboluminescence. Diphenyl-*p*-tolylmethane, the corresponding ortho-compound, and diphenyl-*m*-tolylcarbinol do not show this property.

J. J. S.

Alkylated Aminoacetonitriles. EMIL KNOEVENAGEL (*Ber.*, 1904, **37**, 4073—4087)—[With KARL SCHLEUSSNER].—Anilinophenylacetonitrile is best prepared by warming mandelonitrile with aniline and potassium cyanide or sodium acetate in alcoholic solution. *p*-Toluidinophenylacetonitrile is obtained by a similar method. *o*-Toluidine does not react with mandelonitrile in presence of potassium cyanide at 100° . α -Naphthylaminophenylacetonitrile, prepared from mandelonitrile and α -naphthylamine in presence of potassium cyanide, melts at 106° (Sachs and Goldmann, *Abstr.*, 1902, i, 780).

[With OTTO KLUCKE].—When shaken with aqueous sulphurous acid, benzylideneaniline forms aniline anilinophenylmethanesulphonic acid, $\text{NHPh}\cdot\text{CHPh}\cdot\text{SO}_3\text{H}\cdot\text{NH}_2\text{Ph}$, which crystallises in matted, white needles, melts at 124 — 125° , and is probably identical with Eibner's substance obtained from benzylideneaniline and sulphur dioxide in ethereal solution (*Abstr.*, 1901, i, 378. Compare Speroni, *Abstr.*, 1903, i, 246).

When warmed with potassium cyanide, the aqueous solution of sodium anilinomethanesulphonate, obtained by the action of aniline on formaldehyde dissolved in aqueous sulphurous acid, yields *anilinoacetonitrile*, which melts at 48° . The following substances have been prepared by this method: *p*-toluidinoacetonitrile, which melts at 57° ; *m*-xylidinoacetonitrile, which melts at 50 — 52° ; α -naphthylaminoacetonitrile, which melts at 44 — 45° ; β -naphthylaminoacetonitrile, which melts at 82 — 85° ; *o*-carboxyphenylaminoacetonitrile, which melts and decomposes at 182 — 184° ; *o*-chloroanilinoacetonitrile, which boils at 174 — 175° under 15 mm. pressure, and when hydrolysed yields an acid, $\text{C}_8\text{H}_8\text{O}_2\text{NCl}$, which melts at 166 — 167° and loses CO_2 at 210° .

Piperidinoacetonitrile, $\text{C}_7\text{H}_{12}\text{N}_2$, is obtained by the action of potassium

cyanide on the aqueous solution of *sodium piperidinomethanesulphonate*, formed by the action of piperidine on formaldehyde in aqueous sulphurous acid solution. It is identical with Klages and Margolinsky's compound (this vol., i, 145). In similar manner, *methylanilinoacetonitrile* is obtained from methylaniline; *ethylanilinoacetonitrile*, $\text{NEtPh}\cdot\text{CH}_2\cdot\text{CN}$, which melts at 21° and boils at $150\text{--}151^\circ$ under 13 mm. pressure, from ethylaniline, and *phenylbenzylaminoacetonitrile*, which is a viscid oil, from benzylaniline.

Sodium anilinophenylmethanesulphonate, $\text{NHPh}\cdot\text{CHPh}\cdot\text{SO}_3\text{Na}$, obtained by warming benzylideneaniline with aqueous sodium hydrogen sulphite, decomposes with evolution of sulphur dioxide on acidification, and, when boiled with dilute alcoholic potassium cyanide, forms anilinophenylacetonitrile.

Anilino-o-hydroxyphenylacetonitrile, formed from salicylideneaniline, crystallises in yellow needles, melts at $113\text{--}114^\circ$, and is probably identical with Haarmann's compound from hydrogen cyanide, salicylaldehyde, and aniline (*Ber.*, 1873, 6, 339). Anilino-*p*-isopropylphenylacetonitrile (cumenylanilinoacetonitrile, Miller and Plöchl, *Abstr.*, 1899, i, 127) is obtained from cuminaldehyde and aniline. *Anilino-p-methoxyphenylacetonitrile* crystallises in white needles and melts at $104\text{--}105^\circ$. *Methylanilinophenylacetonitrile*, $\text{NMePh}\cdot\text{CHPh}\cdot\text{CN}$, obtained from methylaniline and benzaldehyde, is identical with Sachs and Goldmann's product from mandelonitrile (*loc. cit.*). *α -Piperidinopropionitrile*, $\text{C}_8\text{H}_{14}\text{N}_2$, is an oil and boils at $93\text{--}94^\circ$ under 12.5 mm. pressure; *α -piperidinophenylacetonitrile* melts at $62\text{--}63^\circ$; *α -piperidino-o-hydroxyphenylacetonitrile* melts at $89\text{--}90^\circ$; *α -piperidino-p-methoxyphenylacetonitrile* melts at $75\text{--}76^\circ$; *α -piperidinostyrylacetonitrile*, from cinnamaldehyde, melts at $98\text{--}99^\circ$. G. Y.

Anilide and Phenetide of Acetylglycollic Acid and of Acetylsalicylic Acid. RICHARD ANSCHÜTZ and W. BERTRAM (*Ber.*, 1904, 37, 3975—3977).—*Acetylglycollylanilide* separates from water in silky needles and melts at $89\text{--}90^\circ$. *Acetylglycollyphenetide* separates from dilute alcohol in glistening needles and melts at $130\text{--}131^\circ$. Acetylglycollic acid is readily hydrolysed by water.

Acetylsalicylylanilide separates from alcohol in glistening needles and melts at $136\text{--}137^\circ$. *Acetylsalicylyphenetide* separates from alcohol in glistening needles and melts at 132° .

The compounds described differ from the acids from which they are derived in not being hydrolysed when boiled with water.

The pharmacological action of the various compounds was examined. A. McK.

Anilides of Oxalic Acid containing Sulphur and their Transformation Products. ARNOLD REISSERT (*Ber.*, 1904, 37, 3708—3733).—The action of phosphorus pentasulphide on oxanilic acid, either alone or dissolved in boiling toluene or xylene, always gives rise to resinous products, but on adding the sulphide to ethyl oxanilate dissolved in boiling xylene, *ethyl thionoxanilate*, $\text{NHPh}\cdot\text{CS}\cdot\text{CO}_2\text{Et}$, is obtained, with a good yield, in the form of an oil; the crude ester is purified with difficulty, and is best converted directly into *thionoxanilic acid*, $\text{NHPh}\cdot\text{CS}\cdot\text{CO}_2\text{H}$, which crystallises from

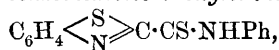
water in bright yellow needles, melts at 101—102°, and gives a *sodium* salt, crystallising in bright yellow leaflets; the *calcium* salt forms needles. The *aniline* salt, $C_{14}H_{14}O_2N_2S$, crystallises in very slender needles and melts and decomposes at 155°, giving rise to a mixture of thioformanilide and diphenylformamidine.

When phosphorus pentasulphide is added to a boiling solution of phenyloxamide in xylene, a mixture of *phenylthionoxamide* and *phenyldithionoxamide* is obtained; the former, $NHPh \cdot CO \cdot CS \cdot NH_2$, crystallises from alcohol in short, thick, straw-coloured prisms and melts at 176°, whilst the latter, $NHPh \cdot CS \cdot CS \cdot NH_2$, crystallises from light petroleum in bright red needles and melts at 98°. On adding potassium ferricyanide to phenyldithionoxamide dissolved in 2½ per cent. aqueous sodium hydroxide, *thionoxanilonitrile*, $NHPh \cdot CS \cdot CN$, is obtained; it is purified by repeatedly dissolving it in aqueous sodium carbonate and precipitating with hydrochloric acid, and forms orange-yellow, woolly needles and melts at 82°. *Thionoxanilamide*, $NHPh \cdot CS \cdot CO \cdot NH_2$, is also formed in this case, but it is best obtained by warming the nitrile with dilute sodium hydroxide solution; it crystallises from alcohol in thick, yellow needles and melts at 169—170°.

When to oxanilide suspended in boiling xylene, phosphorus pentasulphide is added, a mixture of *thionoxanilide*, $NHPh \cdot CS \cdot CO \cdot NHPh$, and *dithionoxanilide*, $C_2S_2(NHPh)_2$, is obtained; the former crystallises from glacial acetic acid in long, thick, yellow needles melting at 144—145°, and the latter forms red or yellow needles according to the nature of the solvent and the concentration of the solution, and gives a colourless, hygroscopic *sodium* salt. *Thionoxanilidesulphonic acid*, $NHPh \cdot CS \cdot CO \cdot NH \cdot C_6H_4 \cdot SO_3H$, obtained by dissolving thionoxanilide in cold concentrated sulphuric acid, gives a *sodium* salt, crystallising in bright yellow leaflets and dissolving in aqueous sodium hydroxide to form, probably, a *disodium* salt, $NPh \cdot C(SNa) \cdot CO \cdot NH \cdot C_6H_4 \cdot SO_3Na$; the structure of the acid follows from its giving anilinesulphonic acid and thionoxanilic acid when boiled with sodium hydroxide solution.

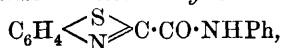
Phenylthionoxamide, $NHPh \cdot CO \cdot CS \cdot NH_2$, by analogy with Sandmeyer's synthesis of indigotin (Abstr., 1903, i, 486), should be convertible, when heated with sulphuric acid, into isatin; but practically the yield is very small. A better result is obtained by the similar treatment of thionoxanilide, when 25 per cent. of the theoretical quantity of isatin is formed.

When thionoxanilide is oxidised by heating it with concentrated or fuming sulphuric acid, *benzothiazolecarboxylic thionanilide*,



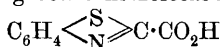
is obtained; it crystallises from glacial acetic acid in soft, golden needles and melts at 155°. When an excess of fuming sulphuric acid (20 per cent. anhydride) is used and the heating prolonged, the *sulphonic acid*, $C_6H_4 \begin{smallmatrix} \text{S} \\ \text{N} \end{smallmatrix} \text{C} \cdot CS \cdot NH \cdot C_6H_4 \cdot SO_3H$, of the anilide is

obtained; the *sodium* salt crystallises from water in leaflets with a bronze-like lustre. *Benzothiazolecarboxylic anilide*,



obtained by oxidising the corresponding thionanilide with alkaline potassium permanganate or by heating benzothiazolecarboxylic acid with aniline at 140—160°, crystallises from alcohol in yellow prisms or white needles and melts at 160°; its *sulphonic acid*, $\text{C}_6\text{H}_4\langle\text{S}\rangle\text{N}\text{C}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, was prepared similarly by oxidising the sulphonic acid of the thioanilide.

Thionoxanilic acid, probably reacting in the form $\text{NPh}\cdot\text{C}(\text{HS})\cdot\text{CO}_2\text{H}$, is readily oxidised by potassium ferricyanide in presence of aqueous sodium hydroxide, forming benzothiazolecarboxylic acid,



(Hofmann, Abstr., 1887, 1040), the sparingly soluble *sodium* salt of which is very characteristic; the *ethyl* ester, $\text{C}_{10}\text{H}_9\text{O}_2\text{SN}$, crystallises from dilute alcohol or light petroleum in voluminous, white needles, melts at 70—71°, and is converted by alcoholic ammonia at 100° into the *amide*, $\text{C}_6\text{H}_4\langle\text{S}\rangle\text{N}\text{C}\cdot\text{CO}\cdot\text{NH}_2$, which crystallises from acetic acid on adding water, melts at 228—230°, and is also obtained by oxidising thionoxanilic amide with an excess of potassium ferricyanide.

W. A. D.

Isomerism of Asymmetric Tollylammonium Salts. II. EDGAR WEDEKIND and F. OBERHEIDE (*Ber.*, 1904, 37, 3894—3898. Compare this vol., i, 732).—*Allyl-o-toluidine*, prepared by the action of allyl iodide on sodium formotoluidide and subsequent hydrolysis, and purified by conversion into its nitroso-derivative, is a yellow oil boiling at 225—230°. Benzyl iodide reacts vigorously with it, forming *benzylallyl-o-toluidine*, a yellow oil, boiling at 180—183° under 27 mm. pressure. The *picrate* forms lemon-yellow needles and melts at 148—150°. The base combines with methyl iodide, forming *benzyl-o-tolylmethylallylammonium iodide*, which separates from alcohol in colourless crystals and melts and decomposes at 154—155°.

Methylallyl-o-toluidine, obtained from methyl-o-toluidine and allyl iodide, distils at 215—220°. The *picrate* crystallises in lemon-yellow needles and melts at 133—135°. The tertiary base combines with benzyl iodide, yielding the quaternary ammonium iodide, which could only be obtained in an amorphous form.

Benzylmethyl-o-toluidine boils at 167° under 13 mm. pressure (compare Rabaut, Abstr., 1892, 313). The *picrate* forms thick, yellow needles melting at 127—128°. The base reacts with difficulty with allyl iodide, and only traces of an amorphous ammonium iodide are obtained.

C. H. D.

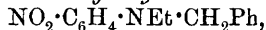
Benzylmalimides. ALBERT LADENBURG and WALTER HERZ (*J. pr. Chem.*, 1904, [ii], 70, 342—344).—A reply to Lutz (this vol., i, 831). G. Y.

Benzylethylaniline. GUSTAV SCHULTZ, G. ROHDE, and EBERHARD BOSCH (*Annalen*, 1904, 334, 235—264. Compare Abstr., 1902, i, 364).—*Benzylethylaniline picrate* melts at 116—117°; *benzylethyl-*

aniline methiodide crystallises in prisms and melts and decomposes at 140.5° . *Benzylethyl-p-nitrosoaniline*, $\text{ON}\cdot\text{C}_6\text{H}_4\cdot\text{NEt}\cdot\text{CH}_2\text{Ph}$, prepared by a method analogous to that used for *p*-nitrosodimethylaniline, forms steel-blue crystals, melts at $61\text{--}62^{\circ}$, and yields benzaldehyde when boiled with concentrated hydrochloric acid. Its *hydrochloride* crystallises in yellow leaflets and melts and decomposes at 116° ; it readily undergoes hydrolytic dissociation.

When benzylethylaniline is nitrated, a mixture of two mono-nitro-derivatives, where the substitution of the nitro-groups occurs in the benzyl residue, is produced. The main product is *m-nitrobenzylethylaniline*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NEtPh}$, which separates from alcohol in reddish-brown prisms and melts at 69° ; its *hydrochloride* forms snow-white prisms and melts at 186° , whilst its *picrate* melts at 131° . When *m*-nitrobenzylethylaniline is oxidised in acetic acid solution by chromic acid, it forms *m*-nitrobenzoic acid. Its constitution was further proved by its synthesis from *m*-nitrobenzylchloride and ethylaniline. *p-Nitrobenzylethylaniline* forms yellow, rhombic crystals and melts at 67° ; its constitution was proved by its synthesis from *p*-nitrobenzyl chloride and ethylaniline. *o-Nitrobenzylethylaniline*, prepared from *o*-nitrobenzyl chloride and ethylaniline, forms brown, rhombic crystals and melts at 66° ; its *hydrochloride* melts at about 158° ; its *platinichloride* melts and decomposes at $116\text{--}117^{\circ}$.

Attempts were made to replace the bromine atom in bromonitrobenzene by the benzylethylamine group. Benzylethylamine (2 mols.) was heated with *o*-bromonitrobenzene (1 mol.) and alcohol for 5 hours at 150° , the product made alkaline with sodium hydroxide and the excess of amine removed by steam distillation, when the residue yielded *benzylethyl-o-nitroaniline*,



as a yellow oil; its *platinichloride*, which melts and decomposes at 176.5° , is not decomposed by water and alcohol, differing in this respect from the platinichloride of the isomeric *o*-nitrobenzyl compound previously described.

Experiments to replace the hydrogen in the amino-group of *m*- and *p*-nitroethylanilines by the benzyl group gave negative results. It was also not found possible to oxidise benzylethyl-*p*-nitrosoaniline to benzylethyl-*p*-nitroaniline by means of potassium permanganate, lead peroxide, potassium persulphate, hydrogen peroxide, ferric chloride, and nitrous acid respectively. *Dinitrobenzylethylaniline*, $\text{C}_{15}\text{H}_{15}\text{O}_4\text{N}_3$, prepared by the action of dilute nitric acid on a solution of benzylethyl-*p*-nitrosoaniline in glacial acetic acid, or by the nitration of benzylethylaniline with fuming nitric acid, separates from alcohol in dark yellow, rhombic crystals and melts at 71° . *Benzylethyl-p-nitroaniline*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NEt}\cdot\text{CH}_2\text{Ph}$, prepared by nitrating a solution of benzylethylaniline in glacial acetic acid by fuming nitric acid, separates from alcohol in dark yellow crystals with blue lustre and melts at 63° . Like dibenzyl-*p*-nitroaniline it does not exhibit basic properties.

Reduction of those mononitrobenzylethylanilines where the nitro-group is substituted in the benzyl group could not be effected.

as-Benzylethyl-p-phenylenediamine, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{Et} \cdot \text{CH}_2\text{Ph}$, prepared by reducing benzylethyl-*p*-nitrosoaniline with zinc dust and sulphuric acid, is a colourless, viscid oil, which boils at 225° under 21 mm. pressure. The *oxalate* crystallises from water in needles and melts at 168 — 169° ; the *benzoyl* derivative crystallises in needles and melts at 131.5° ; the *acetyl* derivative crystallises in needles and melts at 111° .

When an aqueous solution of hydrogen sulphide and then a few drops of ferric chloride are added to a solution of *as*-benzylethyl-*p*-phenylenediamine hydrochloride, a blue coloration appears, owing to the formation of a thiazine dye analogous to methylene-blue.

Benzylethylanilinophenylthiocarbamide melts at 149° . The *azo-dye*, produced by coupling diazotised *as*-benzylethyl-*p*-phenylenediamine with an alkaline solution of β -naphthol, separates from acetone or ethyl acetate in black crystals with a green lustre and melts at 135.5° .

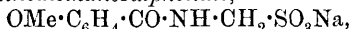
A. McK.

Acylaminomethanesulphonic Salts and their Behaviour to various Potassium Cyanide. EMIL KNOEVENAGEL and HANS LEBACH (*Ber.*, 1904, 37, 4094—4104. Compare this vol., i, 983, 989).—The amides of aromatic carboxylic and sulphonic acids react with formaldehyde and sodium hydrogen sulphite to form sodium acylaminomethanesulphonates. Those derived from sulphonamides react with potassium cyanide to form the corresponding nitriles.

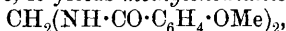
Sodium benzoylaminomethanesulphonate, $\text{NH} \cdot \text{Bz} \cdot \text{CH}_2 \cdot \text{SO}_3\text{Na}$, decomposes without melting when heated above 220° , is easily soluble in water, but only slightly so in alcohol. The *barium* and *lead* salts are insoluble in water, the *silver* salt forms a red precipitate which gradually blackens.

The action of phosphorus pentachloride on the sodium salt under dry ether at 40 — 50° leads to the formation of *s*-dibenzoyldiaminomethane; if the action takes place in absence of a solvent and the product is distilled or treated with ice-water there is obtained a solid substance which melts under warm water and is probably a chloro-derivative of *s*-dibenzoyldiaminomethane.

Sodium anisylaminomethanesulphonate,

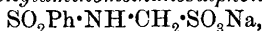


crystallises in colourless needles containing $1\text{H}_2\text{O}$, which is lost at 105° . When treated with phosphorus oxychloride in ethereal solution under reduced pressure, it yields *methylenedianisamide*,



which is also formed from *N*-methylolanisamide, separates from alcohol in white crystals, and melts at 206 — 207.5° .

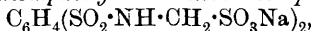
Sodium benzenesulphonylaminomethanesulphonate,



forms an amorphous, white mass and decomposes above 110° with evolution of formaldehyde; it reacts violently with phosphorus pentachloride, but no substance resembling hipparaffin could be obtained. *Benzenesulphonylaminoacetonitrile*, $\text{SO}_2\text{Ph} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CN}$, crystallises in long, colourless, glistening needles and melts at 76 — 77° ; the *potassium* derivative, $\text{SO}_2\text{Ph} \cdot \text{NK} \cdot \text{CH}_2 \cdot \text{CN}$, crystallises in colourless

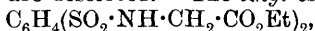
needles. When evaporated with concentrated hydrochloric acid, the nitrile yields *benzenesulphonylaminoacetic acid*, which crystallises in colourless needles and melts at 165—166°.

Sodium benzene-m-disulphonylaminoethanesulphonate,



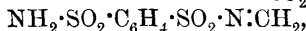
crystallises in small needles.

Benzene-m-disulphonylaminoacetonitrile crystallises in glistening needles and melts at 149—150°. The acid melts and decomposes at 181°; the *ammonium*, *sodium*, *barium*, *calcium*, *magnesium*, *lead*, *copper*, and *zinc* salts are described. The *ethyl ester*,



crystallises in glistening needles and melts at 110°.

Methylenebenzene-m-disulphonamide, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{SO}_2\cdot\text{NH} \\ \text{SO}_2\cdot\text{NH} \end{smallmatrix} \text{CH}_2$, or



formed by the action of formaldehyde on *benzene-m-disulphonamide*, is amorphous, decomposes when heated above 180°, is easily soluble in aqueous alkali hydroxides, and forms a *potassium* derivative crystallising in needles (compare Magnus-Levy, Abstr., 1893, i, 714).

G. Y.

Condensation Products of ψ -Phenols with Dimethylaniline and Analogous Tertiary Bases. KARL AUWERS (*Annalen*, 1904, 334, 264—342. Compare Abstr., 1902, i, 146; 1903, i, 621; this vol., i, 487).—The author has previously shown that primary or secondary bases react with ψ -phenols to form secondary or tertiary amines, the primary base forming a tertiary amine with two aromatic rings. The action of tertiary bases on ψ -phenols is different; with aliphatic tertiary amines, halogen hydride is eliminated, whilst Zincke's methylenequinones are probably formed and undergo immediate polymerisation; tertiary cyclic bases, on the other hand, such as pyridine and quinoline, combine with ψ -phenols to form ammonium salts, the bases corresponding with which are very unstable and yield derivatives of diphenylmethane which do not contain nitrogen.

The condensation products, obtained by the action of dimethylaniline on ψ -phenols, are not salts of quaternary bases, since, by the action of alkali hydroxides, halogen hydride is readily eliminated, whilst compounds are produced having both phenolic and basic characters from which the original condensation product may be regenerated by the action of halogen hydride. Arguments are adduced in favour of those condensation products being regarded as derivatives of diphenylmethane, special reference being made to the constitution of the compound obtained from dimethylaniline and dibromo-*p*-hydroxy- ψ -cumyl bromide.

The action of *as*-dimethyl-*p*-phenylenediamine on dibromo-*p*-hydroxy- ψ -cumyl bromide was studied with the view of finding whether the former acts as a primary or a tertiary amine, and in this way elucidating the nature of the condensation product. It acts exclusively as a tertiary amine, the condensation product yielding, on treatment with acetic anhydride, a monoacetyl derivative, which may also be obtained by the action of the ψ -phenol on acetyl-*as*-dimethyl-*p*-phenylenediamine.

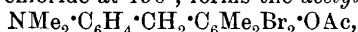
In the condensations under consideration, the halogen hydride salts of dimethylaminodiphenylmethane are first formed and they are converted into the free bases by means of alkali. When the methiodides of those condensation bases are boiled with xylene or acetic anhydride, methyl iodide is eliminated. The insolubility of the bases in aqueous alkali hydroxides is due to the influence of the strongly positive substituents, which mask the slightly acid nature of the phenolic group.

The action of bromine on derivatives of diethylaniline as contrasted with its action on derivatives of dimethylaniline is discussed.

The condensation of dimethylaniline has been studied only in the cases of those ψ -phenols where the negative reactive substituent is a halogen atom, so that it is uncertain whether the formation of diphenylmethane derivatives is general.

[With R. JACOB.]—Experiments were conducted to find out whether the condensation product of dibromo-*p*-hydroxy- ψ -cumyl bromide with dimethylamine was of phenolic or of betaine nature, and whether a double linking was present in its molecule.

3 : 6-Dibromo-4'-dimethylamino-4-hydroxy-2 : 5-dimethyldiphenylmethane (compare Auwers and Avery, Abstr., 1896, i, 150), when heated with acetyl chloride at 150°, forms the *acetyl* derivative,

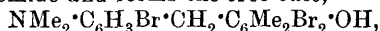


which separates from alcohol in glistening, flat needles, melts at 144—145°, and forms a *hydrochloride* separating from benzene in needles and melting at 270—273°. The *methiodide* of the acetyl derivative separates from a mixture of chloroform and light petroleum and melts at 169—171°. When the methiodide of the free base is acetylated, the acetate of the base is formed.

3 : 6-Dibromo-4-hydroxy-2 : 5-dimethyldiphenylmethane-4'-trimethylammonium hydroxide, $\text{OH} \cdot \text{NMe}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{OH}$ (compare Auwers and Senter, Abstr., 1896, i, 423), prepared by the action of dilute sodium hydroxide on the methiodide of the corresponding amine, crystallises from dilute alcohol in prismatic pyramids and melts at 208°. Its *nitrate* forms transparent, glistening needles and melts and decomposes at 212—214°; its *hydrochloride* forms transparent, tiny needles and melts at 225—226°; its *hydriodide* separates from a mixture of chloroform and light petroleum in rhombic crystals, melts at 190—191°, and is not decomposed when boiled with water. When the methiodide is boiled with xylene, a substance, crystallising partly in needles and partly in prisms, is obtained, which melts at 124° and is identical with the base obtained from dimethylaniline and ψ -cumenol tribromide.

3 : 6-Dibromo-4-hydroxy-2 : 5-dimethyldiphenylmethane-4'-trimethylammonium hydroxide, when acted on by acetic anhydride in the cold, forms transparent leaflets of a *compound* melting at 65—66°, which is probably the acetate of the acetyl derivative. The corresponding *hydrochloride*, $\text{C}_{20}\text{H}_{24}\text{O}_2\text{NClBr}_2$, forms white crystals and melts at 205—207°; by the action of moist silver oxide, it forms the *acetyl* derivative of 3 : 6-dibromo-4-hydroxy-2 : 5-dimethyldiphenylmethane-4'-trimethylammonium hydroxide, $\text{OH} \cdot \text{NMe}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{OAc}$, which crystallises in yellow, hygroscopic leaflets, softening at 95° and decomposing at 120°.

3:6:3'-Tribromo-4-dimethylamino-4-hydroxy-2:5-dimethyldiphenylmethane hydrobromide, prepared by adding bromine to a solution of 3:6-dibromo-4'-dimethylamino-4-hydroxy-2:5-dimethyldiphenylmethane in glacial acetic acid, separates from glacial acetic acid in glistening needles and leaflets and melts at 204°. When boiled with water, it loses hydrogen bromide and forms the free base,

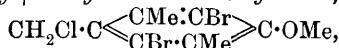


which separates from alcohol in tiny needles and melts at 99—100°. When excess of hydrobromic acid is added to a hot solution of the base in sodium hydroxide, the hydrobromide is again formed. The *acetyl* derivative of the base forms leaflets of a silvery lustre and melts at 156—157°.

[With JOH. REICHEL.]—The incorrectness of the betaine structure, which was originally assigned to the condensation bases, is further shown by the following results.

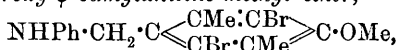
The methoxyl group in the side-chain of dibromo-*p*-hydroxy- ψ -cumyl-alcohol dimethyl ether (compare Auwers and Baum, Abstr., 1897, i, 34) is readily replaced by iodine by the action of hydriodic acid on the ether at the ordinary temperature; the replacement by bromine takes place by the action of hydrobromic acid at 100°, whilst the replacement by chlorine is effected when hydrogen chloride is passed for a long time into a concentrated boiling solution of the ether in acetic acid.

Dibromo-p-hydroxy- ψ -cumyl chloride methyl ether,



separates from glacial acetic acid in glistening needles and melts at 116—117°. *Dibromo-p-hydroxy- ψ -cumyl bromide methyl ether* separates from glacial acetic acid in glistening needles and melts at 122—124°. *Dibromo-p-hydroxy- ψ -cumyl iodide methyl ether* melts at 114—115°.

Dibromo-p-hydroxy- ψ -cumylaniline methyl ether,

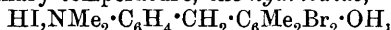


prepared by the addition of aniline to a benzene solution of the preceding iodide, separates from alcohol in glassy needles and melts at 115—116°. The corresponding *piperidine* derivative, $\text{C}_{15}\text{H}_{21}\text{ONBr}_2$, separates from alcohol in glassy plates and melts at 49—51°. *Dibromo-p-hydroxy- ψ -cumylmethylaniline methyl ether*, prepared from the iodide and mono-methylaniline, forms colourless prisms and melts at 90—91°.

Dibromo-p-acetoxy- ψ -cumylmethylaniline, prepared from dibromo-*p*-acetoxy- ψ -cumyl bromide and methylaniline, separates from methyl alcohol in prisms and melts at 102—103°.

When either of the two latter compounds is boiled for 8 hours with an excess of methyl iodide and benzene at 100° in the presence of a little mercury, phenyltrimethylammonium iodide is produced.

When dimethylaniline is condensed with dibromo-*p*-hydroxy- ψ -cumyl iodide at the ordinary temperature, the *hydriodide*,



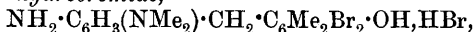
is formed; it crystallises in leaflets of a mother-of-pearl lustre and melts at 220°.

[With O. WEHR.]—*p-Hydroxyphenyltrimethylammonium iodide,*
 $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_3\text{I} \cdot \text{H}_2\text{O},$

prepared by the action of methyl iodide and a concentrated aqueous solution of potassium hydroxide on a solution of *p*-aminophenol hydrochloride in methyl alcohol, melts at temperatures varying between 190° and 201° according to the rapidity of heating; it forms yellow plates. When heated with acetic anhydride in presence of carbon dioxide, it is converted into *acetyl-p-dimethylaminophenol*, $\text{OAc} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$, which crystallises from dilute alcohol in needles or plates and melts at 78—79°. When the latter compound is heated with alcoholic potassium hydroxide, *p*-dimethylaminophenol is produced. *Acetyl-p-dimethylaminophenol methiodide*, $\text{C}_{11}\text{H}_{16}\text{O}_2\text{NI}$, melts at 192—193°.

[With O. WEHR.]—Monoacetyl-*as*-dimethyl-*p*-phenylenediamine is formed when *p*-aminodimethylaniline is mixed with a slight excess of acetic anhydride at the ordinary temperature; when heated with an excess of acetic anhydride, it forms *diacetyl-p-aminodimethylaniline*, which separates from light petroleum in needles and melts at 68—69°; it may also be prepared by heating the free base with an excess of acetic anhydride.

3 : 6-Dibromo-5'-amino-2'-dimethylamino-4-hydroxy-2 : 5-dimethyldiphenylmethane hydrobromide,



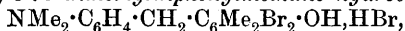
prepared from dibromo-*p*-hydroxy- ψ -cumyl bromide and *p*-aminodimethylaniline, melts at 189—190°; the free base is a dirty yellow powder, melts at 141—142°, and forms a *monoacetyl* derivative, crystallising in glistening, yellow scales and melting at 223—224°; the *diacetyl* derivative separates from alcohol in yellow leaflets and melts at 138—139°.

3 : 6-Dibromo-4'-dimethylamino-4-hydroxy-2 : 5-dimethyldiphenylmethane ethiodide, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{OH}, \text{EtI}$, is a yellowish-white, crystalline powder, which, when quickly heated, melts at 175—176° and, when slowly heated, at 172—173°. When boiled with an alkali hydroxide, it is converted into the base, $\text{C}_{19}\text{H}_{25}\text{O}_2\text{NBr}_2$, which crystallises in white leaflets and melts at 189—190°.

Acetyl 3 : 6-dibromo-4'-diethylamino-4-hydroxy-2 : 5-dimethyldiphenylmethane, $\text{NEt}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{OAc}$, separates from alcohol in glistening scales and melts at 139—140°. Its *methiodide* forms white leaflets and melts at 191—192°. When the free base is brominated, it forms 3 : 6 : 3'-tribromo-4'-diethylamino-4-hydroxy-2 : 5-dimethyldiphenylmethane, which does not crystallise and on exposure becomes tarry.

[With O. HÄHNLE.]—The following compounds were prepared to test whether the phenomena, which were first observed in the ψ -cumenol series, are general for ψ -phenols of the para-series.

If molecular amounts of dibromo-*p*-hydroxymesityl bromide and dimethylaniline are mixed in benzene solution, 2 : 6-dibromo-4'-dimethylamino-4-hydroxy-3 : 5-dimethyldiphenylmethane hydrobromide,



is formed as silky needles, melting completely at 250°. The free base melts at 128°; its *acetate* separates from alcohol in white needles and melts at 145—146.5°; its *methiodide* separates from glacial acetic acid in yellow crystals, melts and decomposes at 193—196°, and forms an *acetyl* derivative which melts and decomposes at 184—185°. The

corresponding *quaternary base*, $\text{OH} \cdot \text{NMe}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{OH}$, prepared by the action of dilute sodium hydroxide on the iodide, forms leaflets or needles of a mother-of-pearl lustre, which soften at 160° and melt at $188-191^\circ$.

2 : 6 : 3'-*Tribromo-4'-dimethylamino-4-hydroxy-3 : 5-dimethyldiphenylmethane hydrobromide*, prepared by bromination of the base melting at 128° , separates from glacial acetic acid in grey leaflets of a fatty lustre and melts at $224-224.5^\circ$. The free *base* separates from dilute alcohol in pink needles and melts at 135° ; its *acetyl* derivative separates from alcohol in glassy needles and melts at $150-151.5^\circ$; its *methiodide* forms yellow needles, melts and decomposes at $172-173^\circ$, and, when boiled with xylene, parts with methyl iodide.

The condensation of dibromo-*p*-hydroxymesityl bromide with diethyl-aniline proceeds similarly to that with dimethylaniline. 2 : 6-*Dibromo-4'-diethylamino-4-hydroxy-3 : 5-dimethyldiphenylmethane hydrobromide* forms silky needles and melts and decomposes at $278-279^\circ$. The free *base* separates from dilute alcohol in rhombic plates and melts completely at $132-133^\circ$.

[With R. ZAUBITZER.]—Whilst *o*- ψ -phenols condense with dimethylaniline quite as readily as do *p*- ψ -phenols; dibromo-*m*-hydroxy- ψ -cumyl bromide does not.

Tetrabromo-*o*-hydroxybenzyl bromide interacts with dimethylaniline to form the *hydrobromide*, $\text{C}_{15}\text{H}_{14}\text{ONBr}_5$, which forms silky needles and melts at $213-214^\circ$. The free *base*, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{Br}_4 \cdot \text{OH}$, separates from a mixture of light petroleum and benzene in pyramids of a diamond lustre and melts at $121-123^\circ$; its *methiodide* forms golden-yellow needles and melts at $165-166^\circ$.

[With WILHELM STRECKER.]—*o*-Bromo-*p*-hydroxybenzyl alcohol, prepared by the action of carbon dioxide on a mixture of *m*-bromophenol, sodium hydroxide, and formaldehyde which had remained at the ordinary temperature for 10 days, forms glistening needles and melts at $137-138^\circ$. When bromine is added to its solution in glacial acetic acid, tribromo-*p*-hydroxybenzyl bromide, melting at 122° , is produced (compare Zincke and Wiederhold, *Abstr.*, 1902, i, 284). When the benzene solution of the latter compound is mixed with dimethylaniline, 2 : 3 : 5-*tribromo-4'-dimethylamino-4-hydroxydiphenylmethane hydrobromide*, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{HBr}_3 \cdot \text{OH} \cdot \text{HBr}$, is produced; it separates from glacial acetic acid in glistening leaflets and melts at $224-225^\circ$. The free *base* crystallises from alcohol in needles and melts at 127° ; its *methiodide* forms a yellow, crystalline powder and melts at $171-173^\circ$.

When *p*-ethylphenol tetrabromide, $\text{CHMeBr} \cdot \text{C} \begin{smallmatrix} \text{CBr} \cdot \text{CBr} \\ \text{CH} - \text{CBr} \end{smallmatrix} \text{C} \cdot \text{OH}$, is condensed with dimethylaniline, it forms 2 : 3 : 5-*tribromo-4'-dimethylamino-4-hydroxy-as-diphenylethane hydrobromide*,

$\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHMe} \cdot \text{C}_6\text{HBr}_3(\text{OH}) \cdot \text{HBr}$, which melts at $202-207^\circ$. The free *base* crystallises from alcohol in needles and melts at 108° ; its *hydriodide* forms glistening, yellow crystals and melts at $183-185^\circ$.

[With WILHELM STRECKER.]—By the partial reduction of 3 : 6-dibromo-4'-dimethylamino-4-hydroxy-2 : 5-dimethyldiphenylmethane by

means of zinc dust and acetic acid, as well as by its reduction by sodium amalgam in alkaline solution, 6-bromo-4'-dimethylamino-4-hydroxy-2 : 5-dimethyldiphenylmethane, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{HMe}_2\text{Br} \cdot \text{OH}$, was produced; it separates from dilute alcohol in pink crystals and melts at 155—157°. When the reduction is conducted with sodium and boiling alcohol, 4'-dimethylamino-4-hydroxy-2 : 5-dimethyldiphenylmethane, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_2\text{Me}_2(\text{OH})$, was produced; this melts at 153—155°.

3 : 5-Dibromo-4'-dimethylamino-4-hydroxydiphenylmethane hydrobromide, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{OH} \cdot \text{HBr}$, prepared from dimethylaniline and dibromo-*p*-hydroxybenzyl bromide, melts at 118—122°; the free base was not obtained pure, but its methiodide forms yellow leaflets and needles of a mother-of-pearl lustre and melts and decomposes at 175°.

When the condensation product formed from dibromo-*p*-hydroxybenzyl bromide and dimethylaniline is dissolved in alcohol, sodium added, and then carbon dioxide passed into the product, from which the alcohol had been removed, 4'-dimethylamino-4-hydroxydiphenylmethane, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$, is precipitated; it separates from light petroleum in glistening prisms and melts at 108—109°. Its benzoyl derivative forms glistening leaflets and melts at 118—118.5°. That the two latter compounds were derivatives of diphenylmethane was also proved by their preparation from 4-amino-4'-diphenylaminodiphenylmethane, obtained from *p*-dimethylaminobenzyl-*p*-toluidine.

A. McK.

Tetrachlorophenol and Pentachlorophenol. HEINRICH BILTZ and WILHELM GIESE (*Ber.*, 1904, 37, 4010—4022. Compare this vol., i, 1021, 1022).—Tetrachlorophenol (Zincke and Schaum, *Abstr.*, 1894, i, 231), obtained by reduction of α -heptachloro-*o*-tetrahydrobenzene with stannous chloride and hydrochloric acid in warm acetic acid solution, contains pentachlorophenol; the two may be separated by fractional distillation, as tetrachlorophenol boils at 150° and pentachlorophenol at 195° under 16 mm. pressure. If, during the reduction, the temperature of the reacting mixture is kept below 10°, tetrachlorophenol only is formed.

2 : 3 : 4 : 6-Tetrachlorophenol melts at 69—70° (Zincke and Walbaum, *Abstr.*, 1891, 710, give the melting point as 67°) and boils at 155° under 18 mm., at 159° under 20 mm., and at 164° under 23 mm. pressure. Hugounenq's compound melting at 152° (*Abstr.*, 1891, i, 297) was chiefly pentachlorophenol.

The sodium derivative, $\text{C}_6\text{HOCl}_4\text{Na}$, crystallises in clusters of white needles and melts at 370°; the acetate, $\text{C}_6\text{H}_4\text{O}_2\text{Cl}_4$, forms small, white crystals and melts at 65—66°; the methyl ether (Hugounenq, *Abstr.*, 1890, 241) crystallises in colourless needles and melts at 64—65°; the ethyl ether crystallises in long needles and melts at 59—60°; the phenylcarbamate, $\text{C}_{13}\text{H}_6\text{O}_2\text{Cl}_4\text{N}$, crystallises in long, colourless needles and melts at 141—142°.

Trichloroquinone, obtained by the action of fuming nitric acid on tetrachlorophenol, melts at 169—170°; trichloroquinol is found to melt at 138°. The action of boiling bromine water on tetrachloro-

phenol leads to the formation of chloranil and oily products. With chlorine in anhydrous acetic acid, tetrachlorophenol yields heptachloroketotetrahydrobenzene.

Pentachlorophenol is best prepared by long boiling of heptachloroketotetrahydrobenzene in acetone solution. The *ethyl ether* crystallises in long, colourless prisms and melts at 89—90°; the *n-propyl ether* crystallises in colourless prisms and melts at 49—50°; the *n-butyl ether* melts at 15·5—16·5° and boils at about 343°; the *benzyl ether* crystallises in long prisms and melts at 167—168°; the *benzoate* crystallises in long, pointed prisms and melts at 164—165°. When chlorinated at the ordinary temperature, pentachlorophenol yields octachloroketotetrahydrobenzene (Zincke and Schaum, *loc. cit.*), but if chlorination takes place at 100° the product is a mixture of hexa- and octa-chloroketotetrahydrobenzenes (Barral, *Abstr.*, 1895, i, 272). G. Y.

Electrolytic Preparation of *p*-Aminophenol. FRIEDRICH DARMSTÄDTER (D.R.-P. 154086).—In the preparation of *p*-aminophenol by the electrolytic reduction of nitrobenzene, the concentrated sulphuric acid may be advantageously replaced by 80 per cent. acid, the nitrobenzene being then in suspension, and not in solution. The diaphragms and other parts of the apparatus are thus less attacked, and the loss of acid by dilution is reduced. An excess of nitrobenzene must be present throughout in order to avoid reduction to aniline. A current density of 6 amperes per sq. dm. is suitable. The method is also applicable to derivatives of *p*-aminophenol. C. H. D.

Anethole Nitrosochloride. ERNST SCHMIDT and A. ADLUNG (*Chem. Centr.*, 1904, ii, 1038; from *Apoth.-Zeit.*, 19, 655—656).—The additive compounds of anethole, esdragole, eugenol, methyleugenol, isoeugenol, methylisoeugenol, and asarone with nitrosyl chloride have been prepared and compared with the products obtained by Wallach's method of preparation by the action of amyl nitrite and hydrochloric acid. In the case of anethole, both methods yield the same nitrosochloride, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}_3\text{H}_5\cdot\text{NOCl}$, melting at 127°; the piperidine compound, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}_3\text{H}_5\cdot\text{NO}\cdot\text{C}_5\text{NH}_{10}$, melts at 107°. The difference of the behaviour of the propenyl and allyl groups towards nitrosyl chloride is similar to that of their behaviour with nitrogen trioxide, but some of the nitrites of the propenyl derivatives appear to be formed more readily than the nitrosochlorides. E. W. W.

Reduction of Unsaturated Phenol Ethers by Sodium and Alcohol. AUGUST KLAGES (*Ber.*, 1904, 37, 3987—4002. Compare this vol., i, 45).—*p*-Propylanisole, obtained by reduction of *p*-propenylanisole with sodium and alcohol, has a sp. gr. 0·94718 at 20°/4° and n_D 1·5045 at 20°.

2-Ethoxy-1- α -hydroxypropylbenzene, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{CHEt}\cdot\text{OH}$, prepared by the action of magnesium ethyl iodide on salicylaldehyde ethyl ether, is a viscid, colourless oil, boils at 129—130° under 15 mm. pressure, and, when strongly cooled, solidifies to colourless crystals. The *phenyl*-

wrethane, $C_{18}H_{21}O_3N$, crystallises in colourless needles and melts at $95-96^\circ$.

o-Propenylphenetole, $OEt \cdot C_6H_4 \cdot CH:CHMe$, is obtained by converting 2-ethoxy-1- α -hydroxypropylbenzene into its *chloride* and heating with pyridine at 120° , and along with γ -o-ethoxyphenylisocrotonic acid by heating salicylaldehyde ethyl ether with propionic anhydride and sodium propionate at 150° . It is a colourless oil, has a pleasant odour, boils at $120-121^\circ$ under 17 mm., or at $230-231^\circ$ under 757 mm. pressure, is volatile in a current of steam, and is reduced, by sodium and alcohol, to *o*-propylphenetole, $OEt \cdot C_6H_4Pr^a$, which is a colourless, mobile liquid and boils at $99-100^\circ$ under 16 mm. or at 213° under 754 mm. pressure.

γ -o-Ethoxyphenylisocrotonic acid, $OEt \cdot C_6H_4 \cdot CH:CH \cdot CH_2 \cdot CO_2H$, crystallises from dilute alcohol, melts at $130-131^\circ$, and is not volatile in a current of steam; the *silver* salt, $C_{12}H_{13}O_3Ag$, is obtained as a white precipitate; the *methyl* ester is an oil. *m*-Ethoxyphenylisocrotonic acid, formed, along with *m*-propenylphenetole, by the action of propionic anhydride and sodium propionate on *m*-ethoxybenzaldehyde at 150° , crystallises in colourless needles and melts at 98° ; the *methyl* ester is a colourless, odourless oil and boils at $175-176^\circ$ under 14 mm. pressure.

m-Propenylphenetole, which is obtained also by heating a mixture of *m*-ethoxybenzaldehyde and magnesium ethyl iodide on the water-bath for some hours, is a mobile oil, has a fruity odour, and boils at $124-125^\circ$ under 16 mm. pressure; the *nitrosochloride* derivative melts at $122-123^\circ$. *m*-Propylphenetole, formed by reduction of *m*-propenylphenetole, is a colourless, mobile oil, boils at $109-110^\circ$ under 15 mm., or at $220-224^\circ$ under 753 mm. pressure, and, when treated with concentrated sulphuric acid, forms a *sulphonic acid*. The *barium sulphonate* crystallises in leaflets and is easily soluble in water; the *sulphonic chloride* is an oil; the *sulphonamide* crystallises in slender needles and melts at 84° .

p-Propylphenetole, obtained by reduction of *p*-propenylphenetole, is a colourless oil, has an odour resembling that of anise, boils at $108-110^\circ$ under 13 mm. pressure, has a sp. gr. 0.9400 at $15^\circ/4^\circ$, and, when cooled with carbon dioxide and ether, solidifies to a colourless, crystalline mass. The *sulphonic acid* crystallises in long, glistening needles and melts at $66-68^\circ$; the *barium* salt is easily soluble in water; the *sulphonamide* crystallises in colourless needles and melts at $97-98^\circ$.

4-Propionyl-2-methylanisole, $OMe \cdot C_6H_3Me \cdot CO \cdot CH_2Me$, formed by the action of propionyl chloride and aluminium chloride on *o*-tolyl methyl ether in light petroleum, solidifies to a crystalline mass, melts at 41° , and boils at $169-171^\circ$ under 25 mm. pressure. The *oxime* crystallises as glistening leaflets, melts at 99° , and forms a *sodium* derivative as small needles.

Reduction of the ketone leads to the formation of *p*-propenyl-*o*-tolyl methyl ether, *p*-propyl-*o*-tolyl methyl ether, and 3- α -hydroxypropyl-*o*-tolyl 6-methyl ether, which is a viscid, colourless oil, boils at 157° under 2 mm., or at 160° under 22 mm. pressure, and has a sp. gr. 1.0419 at $15^\circ/4^\circ$. The *phenylurethane* crystallises in slender needles and melts

at 78°. The *chloride*, when heated with pyridine at 110°, yields 3-propenyl-*o*-tolyl methyl ether, $\text{OMe} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CH} : \text{CHMe}$, which is a colourless oil, boils at 121—123° under 14 mm. pressure, has a sp. gr. 0.9844 at 16°/4° and n_D 1.5570 at 17°, and is oxidised by potassium permanganate to *o*-bromoanisic acid. The *nitrosochloride* forms small crystals and melts at 117°.

3-Propyltolyl 6-methyl ether is an oil, has an odour resembling that of phenol, boils at 222°, and has a sp. gr. 0.9361 at 18°/4° and n_D 1.5111.

2-Propionyltolyl 5-methyl ether melts at 43° and boils at 149—150° under 14 mm. pressure; the *oxime* melts at 94—95°. Reduction of the ketone leads to the formation of 2-propenyl-, 2-propyl-, and 2- α -hydroxypropyl-tolyl 5-methyl ethers.

2- α -Hydroxypropyltolyl 5-methyl ether is an odourless oil, has a burning, sweet flavour, boils at 149—151° under 13 mm. pressure, and has a sp. gr. 1.0478 at 18°/4°. The *phenylurethane* crystallises in colourless needles and melts at 94—95°. When heated with pyridine at 110°, the *chloride* yields 2-propenyltolyl 5-methyl ether, which boils at 119—121° under 13 mm. pressure and has a sp. gr. 0.9849 at 15°/4° and n_D 1.5555 at 15°. The *nitrosochloride*, $\text{C}_{11}\text{H}_{14}\text{O}_2\text{NCl}$, crystallises in small, colourless needles and melts at 108°. The 2-propenyltolyl 5-ether is oxidised by potassium permanganate in alkaline solution to *m*-homoanisic acid.

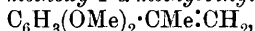
3-Propionyltolyl 4-methyl ether is a colourless oil, boils at 149—151° under 17 mm. pressure, has a sp. gr. 1.0523 at 14°/4°, forms an *oxime* which crystallises in colourless leaflets and melts at 92°, and is reduced by sodium and alcohol to the corresponding carbinol and small amounts of 3-propenyl- and 3-propyl-tolyl 4-methyl ethers. 3- α -Hydroxypropyltolyl-4-methyl ether is a colourless, odourless oil and boils at 153—154° under 22 mm. pressure; the *phenylurethane* crystallises in colourless leaflets and melts at 91°. When heated with pyridine at 120°, the *chloride* yields 3-propenyltolyl 4-methyl ether, which boils at 122—124° under 17 mm. pressure, can be titrated with bromine in carbon disulphide solution, does not yield a *nitrosochloride*, and is oxidised by alkaline potassium permanganate to 4-methoxyisophthalic acid. 3-Propyltolyl 4-methyl ether is a colourless oil, has an odour resembling that of fusel oil, and boils at 216—218°.

p- ψ -Propenylanisole (Béhal and Tiffeneau, Abstr., 1901, i, 272) has a sp. gr. 0.9909 at 40°/0° and is reduced by sodium and alcohol to *p*-isopropylanisole, which boils at 95—96° under 19 mm., or at 212—213° under 756 mm. pressure, has a sp. gr. 0.94952 at 17°/4° and n_D 1.5045 at 17°, and is identical with Paternò and Spica's *p*-isopropylphenyl methyl ether (this Journal, 1877, i, 593).

2 : 5-Dimethoxyacetophenone, $\text{C}_6\text{H}_3\text{Ac}(\text{OMe})_2$, obtained from acetic chloride and quinol dimethyl ether in presence of aluminium chloride, is a viscid oil, which boils at 156—158° under 15 mm. pressure and has a sp. gr. 1.1385 at 20°/4°. The *semicarbazone* crystallises in colourless needles and melts at 181—182°.

2 : 5-Methoxy-1- α -hydroxyisopropylbenzene, $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{CMe}_2 \cdot \text{OH}$, is a colourless oil, which boils at 138—141° under 16 mm. pressure and has a sp. gr. 1.0854 at 25°/4°. When heated with pyridine at 125°,

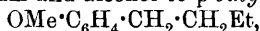
the *chloride* yields 2:5-methoxy-1- α -methylvinylbenzene,



which is a mobile oil, boils at 124—125° under 15 mm. pressure, and has a sp. gr. 1.0382 at 22°/4° and n_D 1.536. *isoPropylquinol dimethyl ether* is a clear oil, boils at 114—116° under 15 mm. pressure, and has a sp. gr. 1.0129 at 17°/4° and n_D 1.5105 at 17°.

α -Methyl-p-propenylanisole, obtained by the action of magnesium ethyl iodide on acetylanisole, boils at 122—123° under 16 mm., or at 233—236° under 760 mm. pressure, has a sp. gr. 0.9827 at 20°/4° and n_D 1.5466. The *dibromide* formed by the action of bromine on methyl propenylanisole in carbon disulphide solution is an oil. *p- α -Methylpropylanisole*, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CHMeEt}$, boils at 106—108° under 16 mm. pressure, has a sp. gr. 0.94336 at 20°/4° and n_D 1.5062.

p- α -Ethylpropenylanisole, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CEt} \cdot \text{CHMe}$, is formed by the action of magnesium ethyl iodide on ethyl anisate; it is a colourless oil, which boils at 129—130° under 17 mm. pressure, has a sp. gr. 0.9684 at 21°/4° and n_D 1.5062 at 20°, and is reduced by sodium and alcohol only with difficulty, as after three reductions the product had a sp. gr. 0.96155 and n_D 1.5273 at 22°. The action of magnesium propyl iodide on anisaldehyde leads to the formation of *p*-butenylanisole (Perkin, this Journal, 1877, ii, 671), which boils at 135—136° under 26 mm. pressure, has a sp. gr. 0.98648 at 15°/4° and n_D 1.5545 at 15°, and is reduced by sodium and alcohol to *p*-butylanisole,



which boils at 120° under 19 mm. pressure, has a sp. gr. 0.9372 at 15°/4° and n_D 1.5027 at 15°, and forms a *sulphonic acid* crystallising in glistening leaflets.

m-Butylolanisole, formed by the action of magnesium propyl iodide on *m*-methoxybenzaldehyde, is a viscid, odourless oil, boils at 151—152° under 15 mm. pressure, and has a sp. gr. 1.0403 at 25°/4°; the *phenylurethane* melts at 63—64°. When heated with pyridine at 125°, the *chloride* yields *m*-butenylanisole, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CHEt}$, which is a mobile oil, boils at 128—129° under 16 mm. pressure, has a sp. gr. 0.987 at 25°/4° and n_D 1.5458 at 25°, decolorises potassium permanganate, and forms an *additive* compound with bromine. *m*-Butylanisole is a mobile oil, has a pleasant odour, boils at 115—116° under 19 mm. pressure, and has a sp. gr. 0.9393 at 22°/4° and n_D 1.5035 at 22°.

o-Butenylphenetole, $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CHEt}$, formed by the action of magnesium propyl iodide on salicylaldehyde ethyl ether, is a colourless oil, boils at 126—127° under 19 mm. pressure, has a sp. gr. 0.97136 at 15°/4° and n_D 1.538 at 15°, decolorises potassium permanganate, forms an *additive* compound with bromine, and dissolves in concentrated sulphuric acid to a reddish-brown solution which, on addition of ice, forms a white, amorphous, flocculent precipitate. *o*-Butylphenetole is a mobile, highly refractive oil, boils at 124—125° under 19 mm. pressure, has a sp. gr. 0.9226 at 15°/4° and n_D 1.496 at 15°, and forms a crystalline *sulphonic acid*.

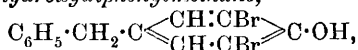
p-isoButenylphenetole, obtained by reducing isobutyrylphenetole (Gattermann, Abstr., 1890, 964) with sodium and alcohol, boils at 128° under 15 mm. pressure, has a sp. gr. 0.9740 at 17°/4° and n_D 1.5472 at 17°, and can be titrated with bromine in carbon disulphide solution.

o-Heptenylanisole, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CH} \cdot \text{C}_5\text{H}_{11}$, formed by the action of

magnesium and *o*-iodoanisole on heptaldehyde, is a viscid oil, boils at 179° under 15 mm. pressure, and has a sp. gr. 0.99268 at $17^{\circ}/4^{\circ}$ and n_D 1.5087 at 17° . *o*-Heptylanisole is a mobile oil, boils at $153-155^{\circ}$ under 20 mm. pressure, has a sp. gr. 0.91854 at $17^{\circ}/4^{\circ}$ and n_D 1.4956, and forms a *sulphonic acid* which crystallises in needles. G. Y.

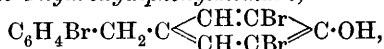
Action of Bromine and Chlorine on Phenols: Substitution Products, ψ -Bromides and ψ -Chlorides. XI. Action of Bromine on 4-Hydroxydiphenylmethane. THEODOR ZINCKE and WILHELM WALTER (*Annalen*, 1904, 334, 367—385. Compare this vol., i, 401).—4-Hydroxydiphenylmethane is readily prepared by the action of benzyl chloride on phenol in the presence of zinc; it forms silky needles and melts at 84° . Its *benzoyl* derivative forms needles and melts at 87° .

3 : 5-Dibromo-4-hydroxydiphenylmethane,



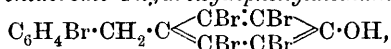
prepared by the gradual addition of the calculated amount of bromine to a cold solution of 4-hydroxydiphenylmethane in chloroform, exists in two crystalline modifications; one forms colourless needles and melts at 44° , the other forms rhombic crystals and melts at 57° . The former variety is unstable and passes readily into the latter on being left at the ordinary temperature. The *acetyl* derivative forms monoclinic prisms and melts at 53° .

3 : 5 : 4'-Tribromo-4-hydroxydiphenylmethane,



was prepared by agitating 4-hydroxydiphenylmethane with an excess of bromine until all had dissolved, and then crystallising the product obtained after removal of the bromine from petroleum, when slender needles, melting at 88° , separated. When its solution in glacial acetic acid is treated with sodium nitrite, one atom of bromine is replaced by one nitro-group. Its *acetyl* derivative melts at 105° .

2 : 3 : 5 : 6 : 4'-Pentabromo-4-hydroxydiphenylmethane, probably



prepared by allowing either 4-hydroxydiphenylmethane, its dibromo- or tribromo-derivative, to remain for a considerable time in presence of excess of bromine, separates from glacial acetic acid in silky needles and melts at $146-147^{\circ}$. The main product of the action consists, however, of ψ -bromides, the presence of which was recognised by their being precipitated as a yellow mass by the addition of water to the glacial acetic acid solution used in washing the pentabromo-compound just described.

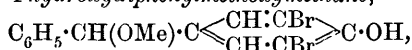
Benzylidene-2 : 6-dibromoquinone, $\text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{C} \begin{array}{c} \text{CH} \cdot \text{CBr} \\ \text{CH} \cdot \text{CBr} \end{array} \text{CO} \cdot \text{H}_2\text{O}$,

prepared by the addition of the calculated quantity of bromine to a solution of dibromo-4-hydroxydiphenylmethane in carbon tetrachloride and then heating the mixture for four hours at 100° , forms a yellow, crystalline powder, which softens at $135-136^{\circ}$. The ψ -bromide was not obtained, and neither a ψ -bromide nor chloride could be prepared from the quinone itself. The latter is very readily transformed into *dibromo*-4-

hydroxydiphenylcarbinol, $C_6H_5 \cdot CH(OH) \cdot C \begin{smallmatrix} \swarrow CH: CBr \\ \searrow CH: CBr \end{smallmatrix} \cdot C \cdot OH$, on simple exposure or by the action of alkali; it is also formed when the quinone in acetone solution is acted on by stannous chloride or bromide or when the quinone is boiled with glacial acetic acid and sodium acetate or with methyl alcohol; it crystallises in white needles which melt to a yellow solution at $164-165^\circ$. Its solution in sodium carbonate or in alkalis is colourless, whilst with sulphuric acid its solution is red, an indication that the quinone is regenerated.

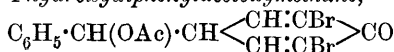
Its *quinone* form, $C_6H_5 \cdot CH(OH) \cdot CH \begin{smallmatrix} \swarrow CH: CBr \\ \searrow CH: CBr \end{smallmatrix} CO$, formed from the hydrated benzylidenedibromoquinone by means of hydrochloric acid, forms leaflets and softens at $137-138^\circ$.

3 : 5-Dibromo-4-hydroxydiphenylmethoxymethane,



prepared by the action of methyl alcohol and sulphuric acid on the preceding compound or on the carbinol, separates from petroleum in white rhombohedra and melts at 126° . Its *acetyl* derivative separates from glacial acetic acid in needles and melts at 97° .

3 : 5-Dibromo-4-hydroxydiphenylacetoxymethane,



or $C_6H_5 \cdot CH(OAc) \cdot C \begin{smallmatrix} \swarrow CH: CBr \\ \searrow CH: CBr \end{smallmatrix} \cdot C \cdot OH$, prepared either from the quinone or from the quinonoidal form of the carbinol, separates from dilute acetic acid in glistening needles and melts at 115° to a yellow solution.

The *acetyl* derivative, $C_6H_5 \cdot CH(OAc) \cdot C \begin{smallmatrix} \swarrow CH: CBr \\ \searrow CH: CBr \end{smallmatrix} \cdot C \cdot OAc$, separates from dilute acetic acid in needles and from benzene in glistening, monoclinic prisms; it melts at 109° .

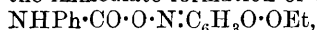
Benzylidenedibromoquinone was reduced by hydriodic acid to dibromo-4-hydroxydiphenylmethane. A. McK.

Two Modifications of α -Nitrosoresorcinol Monoethyl Ether. FERDINAND HENRICH (*J. pr. Chem.*, 1904, [ii], 70, 313—325. Compare Kietabl, *Abstr.*, 1899, i, 343; 1900, i, 163; 1902, i, 447; 1903, i, 88).— α -Nitrosoresorcinol monoethyl ether separates from alcohol in yellow, rhombic crystals, melts at $147-148^\circ$, and, when recrystallised from benzene, toluene, xylene, or carbon disulphide, is converted into the labile *modification*, which separates in green, dichroic crystals and sinters at 127° , changes into the yellow *modification* at $128-130^\circ$, or at $130-140^\circ$ if rapidly heated, and, on further heating, melts at $147-148^\circ$. If formed from the crude ether, it immediately commences to change again into the yellow ether, the change being complete in about a day, but if obtained from the purified ether the reverse change takes place more slowly and may require some weeks for completion.

The action of ethyl iodide on the potassium derivative of α -nitrosoresorcinol monoethyl ether leads to the formation of the *diethyl* ether, $OEt \cdot C_6H_3O : N \cdot OEt$, which forms orange-coloured, crystalline aggregates

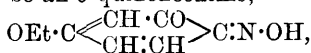
and melts at 89.5—91.5°. When reduced with stannous chloride and hydrochloric acid, it yields the hydrochloride of 5-ethoxy-2-aminophenol.

The action of phenylcarbimide on α -nitrosoresorcinol monoethyl ether dissolved in benzene, alcohol, or other solvent at the laboratory temperature leads to the immediate formation of the *urethane*,

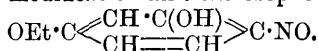


which crystallises in leaflets and, when boiled with alcohol, yields the yellow nitroso-compound. If the reaction is carried out at 6°, it takes place immediately in the alcoholic, but only after 15 minutes in the benzene, solution.

The yellow, stable modification of α -nitrosoresorcinol monoethyl ether is considered to be an *o*-quinoneoxime,



and the green, labile modification an *o*-nitrosophenol,



G. Y.

Action of Nitrous Acid on Resorcinol Monomethyl Ether. FERDINAND HENRICH and HEINRICH EISENACH (*J. pr. Chem.*, 1904, [ii], 70, 332—341. Compare *Abstr.*, 1902, i, 447).—The soluble, brown nitrosoresorcinol monomethyl ether, previously described as melting at 138°, is now found to be impure, labile 2-nitroso-5-methoxyphenol.

The yellow, stable 2-nitroso-5-methoxyphenol forms prismatic crystals; the green, labile nitroso-ether forms dichroic crystals, becomes yellow at 130—140° when rapidly heated, melts at 158—159°, and is slightly more stable than the corresponding ethyl ether. Phenylcarbimide reacts with 2-nitroso-5-methoxyphenol at 7°, immediately in alcoholic, slowly in benzene, solution, to form the *urethane*, $\text{NHPh}\cdot\text{CO}\cdot\text{ON}:\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{OMe}$, which sinters at 162° and melts at 168°.

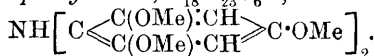
Both the yellow and the green modifications of the methyl ether form the same *sodium* derivative, which, in aqueous solution, has a neutral reaction and yields the yellow ether on acidification. When treated with methyl iodide, the silver derivative yields the dimethyl ether, $\text{OMe}\cdot\text{C}_6\text{H}_3\text{O}:\text{N}\cdot\text{OMe}$, which crystallises in yellow prisms, melts at 115—117°, dissolves in organic solvents to yellow solutions, and, when reduced by stannous chloride and hydrochloric acid, yields 2-amino-5-methoxyphenol.

The constitutional formula $\text{OMe}\cdot\text{C}\begin{array}{c} \text{CH}\cdot\text{CO} \\ \text{CH}:\text{CH} \end{array}\text{C}:\text{N}\cdot\text{OH}$ is ascribed to the yellow, $\text{OMe}\cdot\text{C}\begin{array}{c} \text{CH}\cdot\text{C}(\text{OH}) \\ \text{CH}=\text{CH} \end{array}\text{C}\cdot\text{NO}$ to the green, modification.

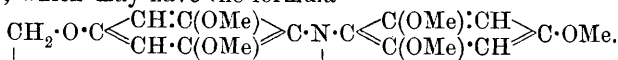
G. Y.

Action of Nitric Acid on Phloroglucinyl Methyl Ether. [HERMANN THOMS and] CARL MANNICH (*Arch. Pharm.*, 1904, 242, 501—512. Compare *Will, Abstr.*, 1888, 457).—The ether can be obtained in good yield by boiling phloroglucinol with methyl alcohol

and concentrated sulphuric acid, isolating the crude product, and methylating it further with 40 per cent. aqueous potassium hydroxide and methyl sulphate. When shaken for an hour or two with 10 per cent. nitric acid at 50—60°, it is converted into dimethoxybenzoquinone. When it is stirred with warm 33 per cent. nitric acid, a blue colouring matter soon separates. This is reduced by sulphurous acid to a colourless substance melting at 142°, which has very feeble basic properties, forms a *nitrosoamine* melting at 193°, and yields the dimethoxyquinone on oxidation; the percentages of C, H, N, and OMe correspond with *hexamethoxydiphenylamine*, $C_{18}H_{23}O_6N$, or



Presumably this is the leuco-base corresponding with the colouring-matter, which may have the formula



The colouring-matter is the *nitrate* of the latter base; when treated with alcoholic potassium hydroxide, it yields the *base* itself,



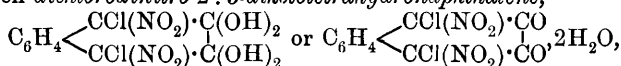
as red needles containing alcohol of crystallisation; only 5 methoxyl groups are now present. When left for 2 days in contact with a solution of potassium hydroxide in dilute alcohol, it is converted into a colourless substance, $C_{17}H_{21}O_5N$, melting at 131—133°, which forms a *nitrosoamine* and generally resembles the leuco-base in appearance and in properties; presumably it is *pentamethoxydiphenylamine*.

C. F. B.

2:3-Dihydroxynaphthalene. THEODOR ZINCKE and K. FRIES (*Annalen*, 1904, 334, 342—366).—By the action of an excess of chlorine on a solution of 2:3-dihydroxynaphthalene in glacial acetic acid, *tetrachloro-2:3-diketotetrahydronaphthalene*, $C_6H_4 \begin{array}{c} \swarrow CCl_2 \cdot CO \\ \searrow CCl_2 \cdot CO \end{array}$, is formed as a white, crystalline powder, which crystallises from a mixture of benzene and petroleum in needles and melts at 115°. It contains $1\frac{1}{2}H_2O$. When reduced by stannous chloride, it forms dichlorodihydroxynaphthalene; when added to nitric acid of sp. gr. 1.5, which is cooled, it dissolves without undergoing oxidation, and, when water is carefully added, the *additive compound*, $C_{10}H_4Cl_4O_2 \cdot HNO_3$, separates in the form of needles, which melt and decompose at 152°. Phthalic acid is produced when tetrachloro-2:3-diketotetrahydronaphthalene is boiled with concentrated nitric acid.

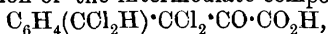
1:4-Dichloro-2:3-dihydroxynaphthalene, $C_6H_4 \begin{array}{c} \swarrow CCl:C \cdot OH \\ \searrow CCl:C \cdot OH \end{array}$, prepared as already indicated or by the chlorination of 2:3-dihydroxynaphthalene, crystallises in colourless prisms and melts at 181°. Its *acetyl* derivative forms small plates and melts at 140.5°. The quinone corresponding with 1:4-dichloro-2:3-dihydroxynaphthalene could not be prepared. When oxidised by boiling with concentrated nitric acid, phthalic acid was formed. It dissolves without decomposition in sodium carbonate and in dilute alkalis. When mixed at the ordinary tem-

perature with five times its weight of nitric acid (sp. gr. 1.4), it dissolves, and then *dichlorodinitro-2:3-diketotetrahydronaphthalene*,

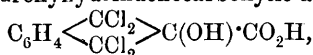


separates; this forms colourless plates, melts and decomposes at 155°, forms phthalic acid when its solution in alkalis is heated, and dissolves in concentrated sulphuric acid with evolution of gas to form a deep blue solution.

Tetrachloroketohydrinden, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CCl}_2 \\ \text{CCl}_2 \end{array} \text{CO}$, formed by the action of bleaching powder on a solution of tetrachloro-2:3-diketotetrahydronaphthalene in glacial acetic acid, forms triclinic pyramids and melts at 98°. Its formation is accounted for by supposing that water is added on to the keto-chloride, when one of the rings is disrupted with the probable formation of the intermediate compound,



which then forms hydroxyhydrindenecarboxylic acid,



from which carbon dioxide and water are eliminated during its oxidation. Tetrachloroketohydrinden is readily converted by alkali hydroxide into phthalidecarboxylic acid, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \text{CH}(\text{CO}_2\text{H}) \end{array} \text{O}$, crystallising in leaflets or needles melting at 153°, and yielding phthalide when heated at about 215°. During its formation, an aldehydic ketonic acid, $\text{CHO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CO}_2\text{H}$, is probably produced as an intermediate product which, by the addition of water, forms a lactonic acid, $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2\text{H}$, which then loses water, being converted into its lactone, phthalidecarboxylic acid.

Phthalonic acid is formed when tetrachloroketohydrinden is acted on by nitric acid of sp. gr. 1.5 at the ordinary temperature.

Dichloro-2:3-naphthaphenazine, $\text{C}_{16}\text{H}_8\text{N}_2\text{Cl}_2$, prepared by the action of *o*-phenylenediamine on tetrachloro-2:3-diketotetrahydronaphthalene in glacial acetic acid solution, separates from chloroform in glistening needles and melts at 265°. Its solution in concentrated sulphuric acid is dark brown; when water is added, an intensely green coloration appears.

It was not found possible to oxidise 2:3-dihydroxynaphthalene to the corresponding quinone.

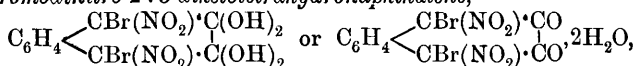
1:4-Dibromo-2:3-dihydroxynaphthalene, prepared by the addition of bromine (2 parts) to a solution of 2:3-dihydroxynaphthalene (1 part) in glacial acetic acid (5 parts), separates from chloroform in colourless needles and melts at 178°. 2:3-Dihydroxynaphthalene is regenerated from it by the action of stannous chloride. When heated with concentrated nitric acid of sp. gr. 1.4, it forms phthalic acid. Its *acetyl* derivative forms glistening leaflets and melts at 175°.

1:4:6:7-Tetrabromo-2:3-dihydroxynaphthalene, prepared by the addition of bromine (5 parts) to a solution of 2:3-dihydroxynaphthalene (1 part) in glacial acetic acid (10 parts), crystallises from chloroform in colourless needles and melts at 242°. It forms 6:7 dibromo-2:3-dihydroxynaphthalene when reduced by stannous chloride

When oxidised by nitric acid of sp. gr. 1.4, it forms 4:5-dibromophthalic acid. Its *acetyl* derivative crystallises in needles and melts at 237°.

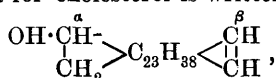
When a concentrated solution of stannous chloride is gradually added to a boiling solution of 1:4:6:7-tetrabromo-2:3-dihydroxynaphthalene (1 part) in glacial acetic acid (20 parts) and the product then acidified by hydrochloric acid, 6:7-dibromo-2:3-dihydroxynaphthalene is formed. It separates from benzene in silvery leaflets and from dilute alcohol in needles, melts at 217°, and is converted by warming with nitric acid of sp. gr. 1.4 into 4:5-dibromophthalic acid. Its *acetyl* derivative forms needles and melts at 155°.

Dibromodinitro-2:3-diketotetrahydronaphthalene,

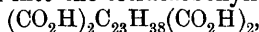


prepared by the addition of 1:4-dibromo-2:3-hydroxynaphthalene (1 part) to nitric acid of sp. gr. 1.51–1.52 (3 parts), separates from benzene in prisms and melts and decomposes at 134°. A. McK.

Cholesterol. III. ADOLF WINDAUS and G. STEIN (*Ber.*, 1904, 37, 3699–3708. Compare this vol., i, 49).—Assuming the formula $\text{C}_{27}\text{H}_{44}\text{O}$ for cholesterol, the authors are of opinion that the molecule consists of a complex of 5 reduced benzene rings; one of these (β) contains a double linking, and another (α) a secondary hydroxyl group. It is probably derived from a 5-ring hydrocarbon related to reduced retene. If the formula for cholesterol is written

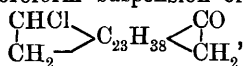


then its transformation into the tetracarboxylic acid,



by the following process is explained.

Phosphorus pentachloride reacts with a chloroform suspension of cholestanonol yielding β -chlorocholestanone,



which crystallises from acetic acid in colourless needles melting at 180–181°; it yields an *oxime* melting at 179–181°, and a *monobromo*-derivative melting at 116–117°. The chlorinated ketone is isomeric with Mauthner and Suida's α -compound melting at 128.5–129° (this vol., i, 50), and is very stable towards all oxidising agents, with the exception of nitric acid, which converts it into the

dibasic acid, $\begin{array}{c} \text{CHCl} \\ \text{CH}_2 \end{array} \text{C}_{23}\text{H}_{38} (\text{CO}_2\text{H})_2$; this crystallises from acetic

acid in needles melting at 243° and is very sparingly soluble in all solvents. Its *ethyl* ester melts at 142–143° and the *anhydride* at 187°. When warmed with 10 per cent. aqueous potash, the chloroacid yields the corresponding *dibasic hydroxy-acid*, $\text{C}_{27}\text{H}_{44}\text{O}_5$, which crystallises from acetone and water in large plates melting, when quickly heated, at 239–240°. It appears to contain 1HO_2 , gives crystalline *magnesium*, *barium*, and *ethyl* salts, and with acetyl chloride

yields the *anhydride*, $C_{27}H_{42}O_4$, which sinters at 210° and melts to a clear liquid at 214° .

The hydroxy-acid, on oxidation with an acetic acid solution of

chromic anhydride, yields the *ketonic acid*, $\begin{array}{c} \text{CO}^\alpha \\ | \\ \text{CH}_2 \end{array} > C_{23}H_{38}(CO_2H)_2$, which is isomeric with the ketonic dibasic acid previously described

(this vol., i, 49) and now represented as $(CO_2H)_2C_{23}H_{38} < \begin{array}{c} \text{CO}^\beta \\ | \\ \text{CH}_2 \end{array}$, as the

carboxylic groups in the two compounds are obtained by the oxidation of different rings of the cholesterol molecule. The new acid crystallises in long, compact needles, melts at about 255° , and is readily soluble in acetone or methyl or ethyl alcohol; the *oxime* melts at 213 – 214° . On oxidation with chromic anhydride, the ketonic acid yields the *tetracarboxylic acid*, $C_{23}H_{38}(CO_2H)_4$, which crystallises from a mixture of ether and benzene in needles, and melts and decomposes at about 174° . It dissolves readily in alcohol, but only sparingly in benzene.

J. J. S.

Products similar to Cholesterol in Bresk from Borneo. J. SACK and BERNHARD TOLLENS (*Ber.*, 1904, 37, 4110–4114).—On subjecting bresk, the product obtained on coagulating the sap of *Alstonia costulata* (*Dryera costulata*), to fractional extraction with alcohol, three crystalline products have been obtained. Using alcohol of 70° Tr. for extraction, a substance *alstol*, $C_{24}H_{38}O$, crystallising in colourless needles melting at 158° is obtained, and having $[\alpha]_D + 56.4^\circ$. *Alstol dibromide* crystallises in yellow platelets melting at 135 – 138° , whilst the *benzoate*, which also crystallises in flat plates, melts at 254° and the *acetate* at 200° . *Alstol* gives most of the colour reactions of the cholesterol group, but is not identical with *isocholesterol*. When the bresk residues are extracted with alcohol of 95° Tr., two other products are obtained. *Alstonin*, $C_{14}H_{22}O$, melts at 191 – 192° and has $[\alpha]_D + 49^\circ$. *isoAlstonin*, $C_{14}H_{22}O$, crystallises in platelets melting at 163° , having $[\alpha]_D + 65.5^\circ$. The bresk residues dissolved in carbon disulphide and purified by precipitation of the impurity with alcohol give, on evaporation, a white, elastic mass, $C_{21}H_{32}O$, melting at 125° .

E. F. A.

Lupeol from the Bark of *Roucheria Griffithiana*. J. SACK and BERNHARD TOLLENS (*Ber.*, 1904, 37, 4105–4109).—The bark of *Roucheria Griffithiana*, when extracted with 85 per cent. alcohol, yields a crystalline product identical with the lupeol obtained by Likiernik (*Abstr.*, 1891, 551) from the husks of *Lupinus luteus*. The product from *Roucheria* melts at 213° (corr.), has the composition $C_{26}H_{42}O$, a molecular weight, determined ebullioscopically, of 430, and $[\alpha]_D + 27.4^\circ$; the *benzoate* crystallises in prisms melting at 262° , the *dibromide* forms colourless platelets melting at 154° . The acetate described by Likiernik could not be obtained. On heating with phenylcarbimide, a compound melting at 226° was formed, having the

composition $C_{26}H_{41}ON$ or $C_{27}H_{41}ON$. After the separation of the lupeol, the mother liquors were proved to contain dextrose.

E. F. A.

Electrolytic Reduction of Aromatic Esters. CARL METTLER (*Ber.*, 1904, 37, 3692—3696. Compare *Tafel*, this vol., i, 849).—When methyl benzoate, dissolved in a mixture of concentrated sulphuric acid, water, and alcohol, is reduced in a divided cell by means of lead electrodes for 6 hours at 15—25° with a current of 15 amperes, the chief products are benzyl alcohol and benzyl methyl ether, $C_6H_5 \cdot CO_2Me + 4H = C_6H_5 \cdot CH_2 \cdot OH + MeOH$ or $= C_6H_5 \cdot CH_2 \cdot OMe + H_2O$.

Probably a compound $C_6H_5 \cdot CH(OH) \cdot OMe$ is first formed. The benzyl alcohol is removed as benzyl hydrogen phthalate by means of phthalic anhydride.

Ethyl benzoate, ethyl *m*-bromobenzoate, and ethyl *o*-chlorobenzoate behave in a similar manner, but the yield of alcohol is much smaller with the halogen compounds. *Benzyl methyl ether* boils at 168°, *benzyl ethyl ether* at 185°, *m*-bromobenzyl ethyl ether at 237°, *o*-chlorobenzyl ethyl ether at 212°, and *o*-chlorobenzyl alcohol crystallises in colourless needles melting at 72°.

J. J. S.

Unsaturated Compounds. F. WILLY HINRICHSSEN (*Annalen*, 1904, 336, 168—227).—The first part of this paper is an elaboration of the author's views published previously (*Abstr.*, 1902, i, 129).

Contrary to Thiele's theory, the formation of additive compounds from a compound containing conjugated ethylene linkings does not result necessarily in addition at the ends of the conjugated system, but is influenced by the electro-chemical characters of the atoms taking part in the reaction, by the relation to each other of the atoms or atomic groupings added, and by substituting groups already present in the unsaturated compound.

[With WILHELM TRIEPEL.]—*Methyl cinnamylideneacetate*,
 $CHPh \cdot CH \cdot CH \cdot CH \cdot CO_2Me$,

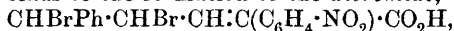
obtained by boiling the acid with methyl alcohol and hydrochloric acid, crystallises in glistening, white scales and melts at 71°.

With hydrogen bromide in ethereal solution, methyl cinnamylidenemalonate forms an *additive* compound, $CHPh \cdot CH \cdot CHBr \cdot CH(CO_2Me)_2$, which loses hydrogen bromide in a desiccator over potassium hydroxide, when heated or when treated with methyl-alcoholic potassium hydroxide; no product could be obtained on reduction, but on oxidation with chromic acid it yields benzoic acid. With sodium ethoxide in ethereal solution, methyl cinnamylidenemalonate forms a hygroscopic *additive* compound, $CHPh \cdot CH \cdot CH(OEt) \cdot CHNa(CO_2Me)_2$, which on hydrolysis yields the original ester and is oxidised by chromic acid to benzoic acid.

The action of ammonia on cinnamylideneacetic acid leads to the formation of the *ammonium* salt which melts at 173° (compare Perkin, *Trans.*, 1877, 31, 403). The acid chloride is not formed by the action of phosphorus pentachloride or thionyl chloride on the acid.

[With MARIE REIMER.]—*α-p-Nitrophenylcinnamylacrylic acid*,
 $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NO}_2)\cdot\text{CO}_2\text{H}$,

obtained from cinnamaldehyde and sodium *p*-nitrophenylacetic acid in presence of acetic anhydride, crystallises in yellow leaflets and melts and decomposes at 258—259°; the *sodium* salt contains $2\text{H}_2\text{O}$; the *methyl* ester crystallises in lemon-coloured needles and melts at 130—131°; the *nitrile*, obtained from cinnamaldehyde and *p*-nitrobenzyl cyanide in presence of sodium ethoxide, crystallises in small, orange-coloured needles and melts at 209—210°. The action of bromine on *α-p*-nitrophenylcinnamylacrylic acid in carbon disulphide solution leads to the formation of the *dibromide*,



which forms yellow crystals and melts at 207—209°. If the bromination is carried out in chloroform solution, a *bromo-δ-lactone* is formed in addition to the dibromide. The *methyl* ester, $\text{C}_{17}\text{H}_{12}\text{O}_4\text{NBr}_2\text{Me}$, melts at 133—135°; the *nitrile* forms yellow crystals and melts at 179—180°.

[With WILHELM TRIEPEL.]—The action of a limited amount of bromine on cinnamylacrylic acid in chloroform solution leads to the formation of a yellow *substance* which melts at 115—120°, and may be a mixture of tetrabromide and unchanged acid. With more bromine, the *tetrabromide*, which crystallises in white needles and melts at 245°, is obtained.

The action of a limited quantity of bromine on the methyl ester in carbon disulphide solution leads to the formation of the *dibromide*, $\text{CHPh}\cdot\text{CH}\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{CO}_2\text{Me}$, which melts at 126° and is oxidised by chromic acid to benzoic acid. The *tetrabromide* crystallises in white needles and melts at 150°.

The *dibromide* of methyl cinnamylidenemalonate forms white crystals and melts at 93°; it reduces silver oxide in alcoholic solution, and is oxidised by chromic acid to dibromocinnamic acid. The *tetrabromide* melts at 135°. The action of hydrogen bromide on the dibromide leads to the formation of a *tribromo-compound*.

The action of bromine on phenylcinnamylacrylic acid in carbon disulphide solution leads to the formation of a substance which melts at 135° and is oxidised to benzoylformic acid (compare Thiele and Rössner, *Abstr.*, 1899, i, 612). G. Y.

A New Method of Esterifying Organic Acids. ALFRED WERNER and W. SEYBOLD (*Ber.*, 1904, 37, 3658—3661).—By the action of methyl sulphate on aqueous solutions of the alkali salts of organic acids, it is possible to obtain the corresponding methyl esters. In this way it is also possible to prepare esters of acids such as 2:4:6-tribromobenzoic acid, which, owing to steric retardation, cannot be esterified by the ordinary methods. The method is applied to acetic, *isovaleric*, stearic, and tribromobenzoic acids; in the last case, a methyl ester melting at 68° was obtained, identical with that previously prepared in small quantities by Wegscheider. *Methyl 2:4:6-trinitrobenzoate* crystallises from alcohol in colourless platelets melting at 158°; *methyl β-methoxy-α-naphthoate* forms colourless crystals melting

at 52°; *methyl β-methoxy-β-naphthoate* crystallises in colourless needles melting at 49°.

E. F. A.

Esterification of Carboxylic Acids by means of Methyl Sulphate. HANS MEYER (*Ber.*, 1904, 37, 4144—4145).—It is pointed out that the method of esterifying carboxylic acids with methyl sulphate, described as new by Werner and Seybold (preceding abstract), was used by Dumas and Peligot so far back as 1835, and subsequently by Wegscheider and by the author.

E. F. A.

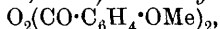
Application of Kolbe's Salicylic Acid Synthesis to Benzene Compounds containing Nitrogen. JOSEF HOUBEN (*Ber.*, 1904, 37, 3978—3981).—Magnesium methyl iodide was added to methylaniline and a current of dry carbon dioxide passed into the product, when the white precipitate of the magnesium compound of methylaniline dissolved. The ethereal solution was then heated at 140—200° for 20 hours. The phenylcarbamate initially formed is transformed under these conditions into *p-methylaminobenzoic acid*, which separates from methylated spirit in red needles and melts at 228—229°.

A. McK.

Transformation of βγ-Unsaturated α-Hydroxy-acids into the Isomeric γ-Ketonic Acids. JOSEF HOUBEN (*Ber.*, 1904, 37, 3981—3983).—A criticism of the views of Erlenmeyer, jun. (this vol., i, 892), respecting the transformation of βγ-unsaturated α-hydroxy-acids into the isomeric γ-ketonic acids when αβ-unsaturated lactones are formed as intermediate products.

A. McK.

Preparation of Anisoyl Peroxide. LUDWIG VANINO and E. UHLFELDER (*Ber.*, 1904, 37, 3624).—*Anisoyl peroxide*,



prepared by the oxidation of a solution of anisoyl chloride in acetone by a mixture of hydrogen peroxide and pyridine at 0°, melts at 128° and explodes on the addition of concentrated sulphuric acid.

A. McK.

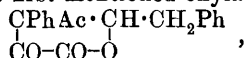
Esterification of Organic Acids. HANS VON LIEBIG (*Ber.*, 1904, 37, 4036—4038. Compare Werner and Seybold, this vol., i, 1013).—The action of methyl sulphate on *m*-dihydroxytriphenylmethanecarboxylic lactone (Abstr., 1903, i, 828) in aqueous potassium hydroxide solution leads to the formation of methyl dimethoxytriphenylmethanecarboxylate, $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CPh}_2\cdot\text{CO}_2\text{Me}$, which crystallises in glistening, rhombic leaflets and melts at 168°, dimethoxytriphenylmethanecarboxylic acid, which crystallises in four-sided prisms and melts at 246°, and hydroxymethoxytriphenylmethanecarboxylolactone, which forms rhombohedric crystals and melts at 181°. The dimethoxy-acid yields the methyl ester when treated with methyl sulphate; it is very stable towards hydrolysing agents, but is partially converted into the monomethoxy-lactone by treatment with boiling acetic chloride.

When treated with ethyl sulphate, dihydroxytriphenylmethanecarboxylolactone yields the ethoxy-lactone and the diethoxy-acid, but no ethyl ester,

G. Y.

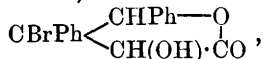
α -Ketonic Acids and their Transformations. EMIL ERLÉNMEYER, jun. (*Annalen*, 1904, 333, 160—227. Compare Abstr., 1902, i, 543).—In this paper, a complete summary of the work carried out in recent years on the α -ketonic acids and the changes which they undergo is given. The mechanism of the reactions of the ketonic acids is discussed from a stereo-chemical standpoint. K. J. P. O.

α -Oxy-lactones and their Transformations. α -Oxy- β -phenyl- γ -benzyl-, α -Oxy- β - γ -diphenyl-, and α -Oxy- β -nitrophenyl- γ -phenylbutyrolactone. EMIL ERLÉNMEYER, jun., and E. ARBENZ (*Annalen*, 1904, 333, 228—237).—To prepare the phenylpyruvic acid required in the preparation of the oxy-lactones, phenylcyanopyruvic acid was boiled with dilute sulphuric acid, α -oxy- β -phenyl- γ -benzylbutyrolactone being produced in considerable amount as a by-product. α -Oxy- β - γ -diphenylbutyrolactone was obtained by condensing phenylpyruvic acid with benzaldehyde in the presence of hydrogen chloride. The *acetyl* derivative of the first mentioned oxy-lactone,



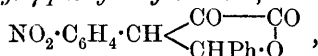
crystallises in needles melting at 91° , whilst the *acetyl* derivative of the oxydiphenylbutyrolactone melts at 115° ; both *acetyl* derivatives yield the original lactones on hydrolysis with hydrochloric acid.

When reduced with zinc and acetic acid, α -oxy- β - γ -diphenylbutyrolactone is converted into desylacetic acid, diphenylcrotonolactone, and an *acid*, $\text{CHPh} \cdot \text{CPh} \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2\text{H}$, which is decomposed on heating with 10 per cent. sodium hydroxide into dibenzyl and oxalic acid. When treated with bromine (1 mol.) in chloroform solution and the solvent carefully evaporated, two bromo-derivatives are obtained; the one is the *dibromide* of the acid, $\text{CHBrPh} \cdot \text{CBrPh} \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2\text{H}$, which crystallises in transparent, rhombic crystals, becoming brown at 140° and decomposing at 144° , and the other is a *bromo-lactone*,



which crystallises in needles resembling asbestos, melting and decomposing at 105° . When boiled with alcohol, both compounds are reconverted into the original oxybutyrolactone.

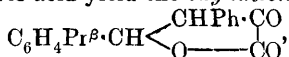
α -Oxy- β -nitrophenyl- γ -phenylbutyrolactone,



is prepared by condensing molecular proportions of benzaldehyde and nitrophenylpyruvic acid by the aid of hydrogen chloride and forms pale yellow, monoclinic crystals melting at 171° , which give a red coloration with alcoholic ferric chloride. The *benzoyl* derivative forms colourless rhombohedra melting at 162° , and the *acetyl* derivative slender needles melting at 118° . K. J. P. O.

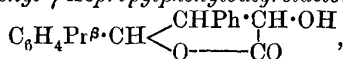
Two Stereoisomeric α -Oxy- β -phenyl- γ -*isopropyl*phenylbutyrolactones and their Transformations. EMIL ERLÉNMEYER, jun., and C. KEHREN (*Annalen*, 1904, 333, 238—254).—Cuminalde

hyde and phenylpyruvic acid yield the *oxy-lactone*,



which crystallises in monoclinic plates [$a:b:c=0.6693:1:0.9101$; $\beta=81^\circ 51'$] melting at 186° . The *acetyl* derivative crystallises in colourless plates melting at 120° , and the *benzoyl* derivative forms prismatic crystals melting at 140° . When the lactone is heated above its melting point, *isopropylstilbene*, $\text{CHPh} \cdot \text{CH} \cdot \text{C}_6\text{H}_4\text{Pr}^\beta$, is obtained as colourless leaflets melting at 85° ; the *diibromide* forms colourless leaflets, becoming brown at 172° and melting and decomposing at 181° .

When reduced with sodium amalgam, the oxy-lactone is converted into α -hydroxy- β -phenyl- γ -isopropylphenylbutyrolactone,



which crystallises in rhombic needles melting at 169° , and when boiled with barium hydroxide yields the α - γ -dihydroxy-acid. On reduction with zinc dust and acetic acid, a γ -ketonic acid,



crystallising in prisms melting at 111° , an unsaturated acid, $\text{C}_6\text{H}_4\text{Pr}^\beta \cdot \text{CH} \cdot \text{CPh} \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2\text{H}$, which crystallises in colourless needles melting at 136° , and an unsaturated lactone are produced. The bromine additive product of the unsaturated acid yields, when boiled with alcohol, the original α -oxy-lactone and its stereoisomeride melting at 198° . The unsaturated lactone, which crystallises in silky needles melting at 124° and is converted into the γ -ketonic acid (m. p. 111°) by boiling with dilute acids or alkalis, is probably represented by the formula $\text{C}_6\text{H}_4\text{Pr}^\beta \cdot \text{C} \begin{array}{l} \text{CPh} \cdot \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{O} \quad \text{CO} \end{array}$, since it yields, when condensed with benzaldehyde in the presence of aniline or piperidine, the

product $\text{C}_6\text{H}_4\text{Pr}^\beta \cdot \text{C} \begin{array}{l} \text{CPh} \cdot \text{C} \cdot \text{CHPh} \\ \diagdown \quad \diagup \\ \text{O} \quad \text{CO} \end{array}$, which crystallises in yellow needles melting at 143° . The unsaturated acid is converted into the lactone and the γ -ketonic acid by boiling with 12 per cent. hydrochloric acid, and quantitatively into the lactone by treatment with acetic anhydride in the presence of sulphuric acid.

The isomeric α -oxy- β -phenyl- γ -p-isopropylbutyrolactone was mainly obtained when the condensation took place at a lower temperature during the winter months, and crystallised in centric groups of needles easily distinguishable from the plates of the isomeride, melting at 198° ; the *acetyl* derivative forms needles melting at 158° , and the *benzoyl* derivative needles melting at 126° .

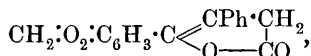
K. J. P. O.

Condensation of Phenylpyruvic Acid with Piperonaldehyde, Cinnamaldehyde, and Furfuraldehyde. EMIL ERLNMEYER, jun., and A. BRAUN (*Annalen*, 1904, 333, 254—268).—When phenylpyruvic acid is condensed with piperonaldehyde in acetic acid solution by means of hydrogen chloride, two isomeric lactones are produced,

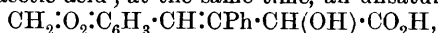
$\text{CH}_2\text{:O}_2 \cdot \text{C}_6\text{H}_5 \cdot \text{CH} \begin{array}{l} \text{CHPh} \cdot \text{CO} \\ \diagdown \quad \diagup \\ \text{O} \quad \text{CO} \end{array}$, which differ in their solubility in

alcohol and in crystalline habit; the more soluble melts at 208° and yields an *acetyl* derivative which crystallises in needles melting at 135° , and a *benzoyl* derivative melting at 179° ; the less soluble melts at 205° , its *benzoyl* derivative at 172° , and its *acetyl* derivative, which crystallises in leaflets, at 130° . The latter lactone is reduced by 4 per cent. sodium amalgam to the corresponding α -hydroxy-lactone, which crystallises in needles melting at 153° , and forms an *acetyl* derivative crystallising in leaflets melting at 116 – 117° . On reducing the lactone, melting at 208° , with sodium amalgam, a *hydroxy-lactone*, which crystallises in needles melting at 155° , is produced; its optical behaviour distinguishes it from the hydroxy-lactone (m. p. 153°) just mentioned.

When the hydroxylactone (m. p. 153°) is boiled for ten hours with dilute hydrochloric acid, it is converted into a γ -ketonic acid, $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\text{:CO}\cdot\text{CHPh}\cdot\text{CH}_2\text{:CO}_2\text{H}$, which forms pale yellow, prismatic crystals melting at 157° ; if the boiling is only continued for five hours, an unsaturated lactone, $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\text{:CH} < \begin{smallmatrix} \text{CPh}\cdot\text{CH} \\ \text{O} \text{---} \text{CO} \end{smallmatrix}$ or



is produced, crystallising in leaflets melting at 183° . The same lactone is also produced when the insoluble lactone (m. p. 205°) is reduced with zinc and acetic acid; at the same time, an unsaturated acid,

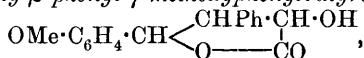


is obtained as a crystalline powder melting at 147° . When boiled with hydrochloric acid, this acid yields both the unsaturated lactone (m. p. 183°) and the γ -ketonic acid (m. p. 157°) just described.

Phenylpyruvic acid condenses with cinnamaldehyde forming an α -oxylactone, $\text{CHPh}\cdot\text{CH}\cdot\text{CH} < \begin{smallmatrix} \text{CHPh}\cdot\text{CO} \\ \text{O} \text{---} \text{CO} \end{smallmatrix}$, which crystallises in needles melting at 179° . No definite substance was isolated from the condensation product of furfuraldehyde and phenylpyruvic acid.

K. J. P. O.

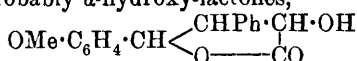
α Oxy- β -phenyl- γ -methoxyphenylbutyrolactone and its Transformations. EMIL ERLNMEYER, jun., and A. LATTERMANN (*Annalen*, 1904, 333, 268–276).—Phenylpyruvic acid and anisaldehyde yield the α -oxy- β -phenyl- γ -methoxyphenylbutyrolactone,



which forms crystals melting at 191° . The *benzoyl* derivative forms needles melting at 170° , and the *acetyl* derivative aggregates of needles melting at 116° . When heated above its melting point until gas ceases to be evolved, the lactone is converted into *p*-methoxystilbene, $\text{CHPh}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, which crystallises in colourless leaflets melting at 135° ; its *dibromide* melts at 177° and loses bromine on recrystallisation.

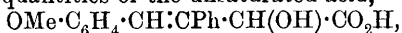
On reduction with sodium amalgam, the α -oxy-lactone is converted into two isomeric substances: a sparsely soluble substance melting at 155° and a readily soluble compound melting at 123° ; both are

neutral, and are probably α -hydroxy-lactones,

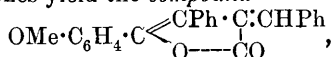


The *acetyl* derivative of the hydroxy-lactone (m. p. 123°) crystallises in needles melting at 117° . When boiled with hydrochloric acid, the hydroxy-lactone is converted into the corresponding γ -ketonic acid, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, which forms crystals melting at 148° .

When reduced with zinc dust and acetic acid, the α -oxy-lactone yields but small quantities of the unsaturated acid,



which melts at 145° , but is mainly converted into two unsaturated lactones melting respectively at 122° and 105° ; the lactone melting at 105° is transformed into that melting at 122° by prolonged heating with acetic anhydride or by the action of an alcoholic solution of aniline. Both lactones are converted into the γ -ketonic acid (m. p. 148°) by heating with sodium hydroxide. When condensed with benzaldehyde, both lactones yield the *compound*

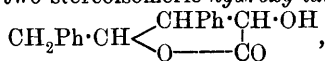


which crystallises in orange-yellow needles melting at 195° ; hence the

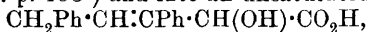
lactones are represented by the formula $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \begin{array}{l} \diagup \text{CPh} \cdot \text{CH}_2 \\ \diagdown \text{O} \text{---} \text{CO} \end{array}$.

K. J. P. O.

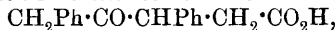
α -Oxy- β -phenyl- γ -benzylbutyrolactone and its Transformations. EMIL ERLÉNMEYER, jun., and E. REIS (*Annalen*, 1904, 333, 276—283).— α -Oxy- β -phenyl- γ -butyrolactone is reduced by 4 per cent. sodium amalgam to two stereoisomeric *hydroxy-lactones*,



which are separated by crystallisation from chloroform; the more sparingly soluble compound forms crystals melting at 153° , whilst the more easily soluble crystallises in needles melting at 113° . Both are unchanged by boiling with 20 per cent. hydrochloric acid, and both yield the same *acetyl* derivative on treatment with acetic anhydride; the latter crystallises in needles melting at 142° and is converted on hydrolysis into the hydroxy-lactone (m. p. 153°). When reduced with zinc dust and acetic acid, the oxy-derivative is converted into the hydroxylactone (m. p. 153°) and into an unsaturated acid,



crystallising in needles melting at 128° ; by boiling with hydrochloric acid, it is transformed into the isomeric ketonic acid,



which melts at 128° .

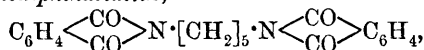
Since it was possible that in the reduction of the α -oxy-lactone α -hydroxy-lactone was formed as an intermediate product, which then was converted into unsaturated acids, an attempt was made to obtain the unsaturated acid from the α -hydroxy-lactone (m. p. 153°) by prolonged boiling with zinc acetate and acetic acid. The hydroxy-lactone

was recovered unchanged; hence the hydroxy-lactone is a by-product and not an intermediate stage.

K. J. P. O.

Conversion of Piperidine into Pentamethylenediamine (Cadaverine). JULIUS VON BRAUN (*Ber.* 1904, 37, 3583—3588).—Benzoylpiperidine yields $\alpha\epsilon$ -dichloropentane with phosphorus chloride (this vol., i, 918). This may then be combined with phthalimide, and the product yields pentamethylenediamine (cadaverine) on hydrolysis.

Pentamethylenediphthalimide,



prepared by heating crude dichloropentane (containing benzonitrile) with potassium phthalimide at 200° , crystallises from alcohol and chloroform in long, felted, slightly yellow needles and melts at 186° . It dissolves sparingly in solvents with the exception of hot chloroform. It dissolves in potassium hydroxide solution, and acids then precipitate *pentamethylenediphthalamidic acid*, $\text{C}_5\text{H}_{10}(\text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H})_2$, which is difficult to purify, but may be precipitated from its alcoholic solution by ether as a white, crystalline powder, melting and decomposing into water and the phthalimide at 156° .

Concentrated hydrochloric acid hydrolyses the phthalimide at 200° to pentamethylenediamine, $\text{NH}_2 \cdot [\text{CH}_2]_5 \cdot \text{NH}_2$, which is identified by means of its salts. The *benzenesulphonyl* derivative, $\text{C}_5\text{H}_{10}(\text{NH} \cdot \text{SO}_2\text{Ph})_2$, separates from alcohol in colourless, glistening crystals and melts at 119° .

C. H. D.

Formyl-*p*-aminophenylglycine. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 154556).—Formylphenylglycine may be nitrated in the same manner as acetylphenylglycine (this vol., i, 806).

*Formyl-*p*-nitrophenylglycine* crystallises from glacial acetic acid in brownish-yellow tablets, melts and decomposes at 159 — 160° , and dissolves in alkalis to a pale yellow solution. *Formyl-*p*-aminophenylglycine*, obtained by reduction, is very soluble in water and has not been isolated in the solid state. Its diazonium compounds may be employed for the preparation of dyes.

C. H. D.

Preparation of Indigotin. KALLE & Co. (D.R.-P. 154524).—Sulphophenylglycinecarboxylic acid is converted into indigo-white by fusion with sodamide. The temperature required is lower than when alkali hydroxides are employed, the removal of the sulpho-group being complete at 200 — 220° .

C. H. D.

Bromination of Indigotin. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 154511. Compare this vol., i, 57, 167).—In the bromination of indigotin in sulphuric acid solution, the acid may be employed of as low a strength as 40 per cent., or even less if a limited quantity is used. A large excess of dilute sulphuric acid, however, causes the formation of bromoisatin. The bromoindigotin prepared in this way is identical with that obtained by dry bromination.

C. H. D.

Brominated Homologues of Indigotin. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 154338. Compare this vol., i, 57, 167).—The homologues of indigotin may be brominated in the presence of mineral acids. The products contain the bromine in the nucleus, and form blue powders with coppery lustre, dissolving fairly readily in organic solvents. *Bromo-* and *dibromo-o-tolyindigotin* and *bromo-* and *dibromo-m-xylyindigotin* are described. C. H. D.

Compounds from Lichens. XII. WILHELM ZOPF (*Annalen*, 1904, 336, 46—85. Compare Abstr., 1895, i, 297; 1896, i, 103; 1897, i, 362, 436; 1898, i, 89, 489; 1899, i, 716; 1901, i, 87, 546; 1902, i, 465, 788; 1903, i, 762).—*Lepranthra impolita* (*Arthonia pruinosa*) has been obtained from an oak barn door at Eckern in Oldenburg. The dark olive-green ethereal extract contains lecanoric acid, lepranthin, and lepranthaic acid.

Lepranthin, $C_{25}H_{40}O_{10}$, crystallises in thin, colourless, monoclinic plates [$a : b : c = 2.4017 : 1 : 0.9273$; $\beta = 16^\circ 57' 40''$], melts at 183° , has $[\alpha]_D + 71^\circ$ at 17° , and is easily soluble in alcohol, ether, or benzene, but only slightly so in light petroleum; the alcoholic solution has a neutral reaction and gives no coloration with ferric chloride.

Lepranthaic acid, $C_{20}H_{32}O_{12}$, crystallises in quadratic plates, melts at 111 — 112° , is moderately soluble in ether, alcohol, or hot benzene, and dissolves easily in sodium hydrogen carbonate solution, from which it is reprecipitated on addition of hydrochloric acid; its solutions in aqueous alkali hydroxides lather like soap solutions; it is not changed when heated with absolute alcohol in a sealed tube for three quarters of an hour at 155 — 160° .

Evernia illyrica, obtained from Dalmatia and Istria, contains 5.5 per cent. of divaricatic acid and almost 0.5 per cent. of atranoric acid, but neither usnic nor evernic acids.

The yellow colour of *Pertusaria Wulfenii* (*P. sulfurea*, *P. sulphurella*, *P. fallax*, &c.), as of *P. lutescens* (Abstr., 1901, i, 547), is due to the presence of thiophanic acid. The extract contains also a small amount of a white, crystalline substance.

Diploicia canescens (*Catolechia canescens*; *Buellia canescens*), obtained from the sandstone walls of a castle in Bentheim, Westphalia, was partly sterile. When washed with aqueous sodium hydrogen carbonate solution, the ethereal solution yields a crystalline precipitate of diploicin (0.75 per cent.) and catolechin (0.01 per cent.); on evaporation of the ethereal filtrate, atranoric acid (0.3 per cent.) and a small amount of an amorphous, brown powder insoluble in benzene are obtained.

Diploicin forms sheaves of brown, thick crystals, melts at 225° , is only slightly soluble in alcohol, ether, glacial acetic acid, or benzene, has only a slight tendency to redden litmus paper, and gives no coloration with ferric chloride.

Catolechin crystallises in long, slender, white needles, softens at 210° , melts at 214 — 215° , is slightly more soluble in benzene than is diploicin, does not redden litmus paper, and gives no coloration with ferric chloride. Diploicin and catolechin are insoluble in aqueous alkali hydroxides or in concentrated sulphuric acid.

Phlyctis argena, from ash trees in Oldenburg, contains salazinic acid.

Cetraria nivalis contains usnic acid, but no protolichestic, protocetraric, nor cetraric acid.

Cetraria stuppea, from Lengerich in Westphalia, contains protolichestic acid and a substance which forms granular crystals, melts at 197—198°, and is not soluble in aqueous sodium hydrogen carbonate solution.

Contrary to Hesse's statement (Abstr., 1902, i, 68), *Cetraria aculeata* (*Cornicularia aculeata*) contains protolichestic acid and no rangiformic acid.

Cladonia squamosa (var. *ventricosa*), obtained from granite blocks in Achtermann, Oberharz, contains squamatic acid (Hesse, Abstr., 1901, i, 150) and usnic acid.

Xanthoria lychnea, var. *pygmæa* (*X. candelaria*; *X. controversa*; *X. parietina*, var. *lychnea*) was gathered from old beams of sennhuts at the Ferrare Alpe on the Grödener Joch and from the Regensburger Hutt. It contains parietin (1.5 per cent.), which crystallises in orange-coloured, slender needles and melts at 202°, but not chrysophanic acid, which melts at 162°.

The occurrence of parietin in *Gasparrinia elegans* (*Amphiloma elegans*; *Placodium elegans*; *Physcia elegans*) (Thompson, *Annalen*, 1845, 53, 266) is confirmed; no rhizocarpic acid could be detected.

Lecidea aglaetora (*L. armeniaca*, var. *lutescens*) contains roccellic acid (6½ per cent.) and cetraric acid (0.9 per cent.).

Contrary to Hesse's statement (Abstr., 1901, i, 149), *Usnea florida* contains usnic acid, hirtellic acid, and a substance which crystallises in spherical aggregates of needles, melts at about 200°, dissolves in sodium hydroxide solution or concentrated sulphuric acid with an intense yellow colour, but neither usnaric, atranoric, nor hirtic acid.

G. Y.

Purification of Aromatic Aldehydes. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 154499).—Sulphurous acid may be employed for the purification of aromatic aldehydes instead of alkali hydrogen sulphites, as it readily dissolves aldehydes, leaving the hydrocarbons and other impurities undissolved. No alkali is needed to decompose the solution, gentle heating at 100° or the passage of a current of air being sufficient to expel the sulphur dioxide. Potassium chloride precipitates the potassium hydrogen sulphite compounds from the solution.

C. H. D.

Oxidising Chlorination of *o*- and *p*-Hydroxybenzaldehydes. HEINRICH BILTZ (*Ber.*, 1904, 37, 4003—4010. Compare Abstr., 1902, i, 162).—The action of chlorine on *p*-hydroxybenzaldehyde in acetic acid solution at 100° leads to the formation of α -heptachloroketotetrahydrobenzene, $\text{CCl}_2 \begin{array}{c} \text{CHCl} \cdot \text{CCl}_2 \\ \text{CCl} = \text{CCl} \end{array} \text{CO}$ (Zincke, Abstr., 1894, i, 231), on salicylaldehyde, to the formation of α -heptachloroketotetrahydrobenzene and chloranil. If the chlorination is carried out in anhydrous acetic acid solution, or at 50—55°, dichlorosalicylaldehyde

is formed, at 80° , at first *dichlorosalicylaldehyde*, and, after eight hours, a small amount of the heptachloroketone are formed. When heated to 180° , the heptachloroketone loses 1 mol. of hydrogen chloride and forms hexachloroketodihydrobenzene; at temperatures above 200° , perchlorophenylene oxide, $(C_6Cl_4O)_x$, which melts at $325\text{--}326^\circ$, is formed.

α -Heptachloroketotetrahydrobenzene is easily reduced by stannous chloride and hydrochloric acid to pentachlorophenol, which melts at $190\text{--}191^\circ$. When warmed with concentrated nitric acid, the heptachloroketone yields chloranil (compare this vol., i, 1000, and following abstracts).
G. Y.

Chlorination of Salicylaldehyde. HEINRICH BILTZ and KARL STEFF (*Ber.*, 1904, 37, 4022—4031. Compare foregoing abstract).—5-Chlorosalicylaldehyde (Bradley and Dains, *Abstr.*, 1892, 1458; Visser, *Abstr.*, 1898, i, 202) is obtained by the action of chlorine on salicylaldehyde warmed on the water-bath. The *phenylhydrazone*, $C_{16}H_{11}ON_2Cl$, crystallises in long, flesh-coloured needles and melts at 148° ; the *semicarbazone*, $C_8H_5O_2N_3Cl$, crystallises in long, white needles and melts and decomposes at $286\text{--}287^\circ$. When boiled with acetic anhydride, the oxime yields 5-chloro-2-acetoxybenzonitrile, $OAc \cdot C_6H_3Cl \cdot CN$, which crystallises in thick, white, transparent needles and melts at $79\text{--}80^\circ$. 5-Chlorosalicylonitrile crystallises in thin, brown needles and melts at $165\text{--}167^\circ$; 5-chloro-2-hydroxybenzamide crystallises in small, white leaflets and melts at $226\text{--}227^\circ$ (compare Smith, *Ber.*, 1878, 11, 1227). The acid, obtained on hydrolysis of the nitrile, crystallises in small, white needles and melts at 168° . When heated with concentrated sulphuric acid, the nitrile yields *p*-chlorophenol.

3:5-Dichlorosalicylaldehyde, $OH \cdot C_6H_2Cl_2 \cdot COH$, is formed when salicylaldehyde is persistently chlorinated in anhydrous acetic acid or chloroform solution at 100° ; it crystallises in yellow prisms, melts at 95° , is easily soluble in the usual organic solvents, forms yellow *sodium* and *ammonium* derivatives, and is decomposed by warm concentrated sulphuric or nitric acids. The *phenylhydrazone* crystallises in yellow, rhombic plates and melts at 153° ; the *semicarbazone* crystallises in silky, yellow needles and melts at 227° ; the *oxime* crystallises in colourless, silky needles and melts at $195\text{--}196^\circ$. 3:5-Dichloro-2-acetoxybenzonitrile, formed by boiling the oxime with acetic anhydride, crystallises in long needles and melts at 78° ; 3:5-dichlorosalicylonitrile forms short needles and melts at 139° . 3:5-Dichlorosalicylic acid melts at 219° (Zincke and Walbaum, *Abstr.*, 1891, 708). When heated with concentrated hydrochloric acid in a sealed tube at 250° , 3:5-dichloro-2-acetoxybenzonitrile yields *o-p*-dichlorophenol.
G. Y.

***m*-Chloro-*p*-hydroxybenzaldehyde.** HEINRICH BILTZ (*Ber.*, 1904, 37, 4031—4036. Compare foregoing abstracts).—*m*-Chloro-*p*-hydroxybenzaldehyde is formed by the action of chlorine (1 mol.) on *p*-hydroxybenzaldehyde (1 mol.) in an ice-cooled saturated chloroform solution. It crystallises in long, white, slender needles, melts at 139° , and boils at $149\text{--}150^\circ$ under 14 mm. pressure (compare Peratoner and Ortoleva, *Abstr.*, 1898, i, 643). The *semicarbazone* crystallises

in long, slender, yellow needles and melts and decomposes at 210° ; the *oxime* crystallises in long, white needles and melts at $144-145^{\circ}$; the *acetate* of the nitrile, $\text{OAc}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CN}$, crystallises in colourless leaflets and melts at $89-90^{\circ}$. *m*-Chloro-*p*-hydroxybenzonitrile crystallises in white needles and melts at 155° ; *m*-chloro-*p*-hydroxybenzamide crystallises in needles and melts at $176-178^{\circ}$; *m*-chloro-*p*-hydroxybenzoic acid melts at 169° (Lössner, this Journal, 1876, ii, 282). *mm*-Dichloro-*p*-hydroxybenzaldehyde (Auwers and Reis, Abstr., 1897, i, 53) melts at $158-159^{\circ}$; the *semicarbazone* crystallises in matted, green needles and melts and decomposes at $236-237^{\circ}$. G. Y.

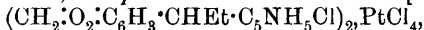
Behaviour of *N*-Alkyl Aldoximes towards Benzenesulphonic Chloride, Phthalyl Chloride, and Picryl Chloride. ERNST BECKMANN [and R. DÜTSCHKE] (*Ber.*, 1904, 37, 4136-4139).—*N*-Benzylbenzaldoxime is converted by the action of benzenesulphonic chloride in benzene solution at water-bath temperature into benzylbenzamide; in addition, ammonium benzenesulphonate and *tribenzylamine benzenesulphonate* are formed in small quantity; the latter forms glistening needles melting at 200° . In alkaline solution, benzylaldoxime is converted almost entirely into benzylbenzamide. From *N*-benzylanisaldoxime, either in benzene or alkaline solution, benzylanisamide was formed by the action of either benzenesulphonic, phthalyl, or picryl chlorides. These results are interpreted as showing that the rearrangement of oximino-compounds to amides is in the main an instance of catalytic change. E. F. A.

Action of Magnesium Ethyl Iodide on Piperonaldehyde. New Synthesis of *iso*Safrole. EFISIO MAMELI (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 315-323. Compare this vol., i, 668).—The action in the cold of magnesium ethyl iodide (1 mol.) in ethereal solution on piperonaldehyde leads to the formation of ethylpiperonyl alcohol, which, when heated, loses a molecule of water yielding *isosafrole*. On oxidising ethylpiperonyl alcohol by means of chromic acid, it gives piperonyl ethyl ketone (propiopiperone), the constitution of which must hence be $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{COEt}$ (compare Wallach and Pond, Abstr., 1896, i, 94).

Ethylpiperonylcarbinol [α :3:4-methylenedioxyphenylpropyl alcohol], $\text{CH}_2\begin{array}{c} \text{O}\cdot\text{C}\cdot\text{CH}\cdot\text{CH} \\ \diagup \quad \diagdown \\ \text{O}\cdot\text{C}\cdot\text{CH}\cdot\text{C}\cdot\text{CHEt}\cdot\text{OH} \end{array}$ is an oily liquid which boils at $172-175^{\circ}$ under 20 mm. pressure, has a faint odour recalling that of *isosafrole*, and is soluble in benzene, ether, chloroform, alcohol, acetic acid, or pyridine; it has a sp. gr. 1.189 at $0^{\circ}/15^{\circ}$. It has the normal molecular weight in freezing benzene, and, on boiling, decomposes into water and the corresponding unsaturated hydrocarbon. Its *acetyl* derivative, $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CHEt}\cdot\text{OAc}$, is a white, oily liquid with a faint pleasant acetic odour and boils at $182-185^{\circ}$ under 12 mm. pressure.

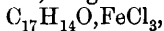
Chlorodihydroisosafrole [α -chloro- α :3:4-methylenedioxyphenylpropane], $\text{CH}_2\begin{array}{c} \text{O}\cdot\text{C}\cdot\text{CH}\cdot\text{CH} \\ \diagup \quad \diagdown \\ \text{O}\cdot\text{C}\cdot\text{CH}\cdot\text{C}\cdot\text{CHEtCl} \end{array}$, prepared by passing dry hydrogen chloride into a cold ethereal solution of piperonyl ethylcarbinol, is an

unstable, oily liquid not capable of being purified by distillation. It combines with pyridine, giving a *compound* separating in tufts of straw-yellow crystals; the *platinichloride* of this compound,

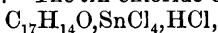


begins to turn brown at 170° and melts and decomposes at $180\text{--}185^\circ$; the *aurichloride*, $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_3\cdot\text{CHEt}\cdot\text{C}_5\text{NH}_5\text{Cl}, \text{AuCl}_3$, blackens at 135° and melts and decomposes at $140\text{--}145^\circ$. T. H. P.

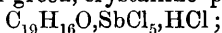
Compounds of Unsaturated Ketones with Metallic Chlorides. ARTHUR ROSENHEIM and WALTER LEVY (*Ber.*, 1904, 37, 3662—3671).—Cinnamaldehyde, when mixed with antimony chloride in chloroform solution, forms a compound, $\text{C}_9\text{H}_8\text{O}, \text{SbCl}_5$, crystallising in glistening, colourless crystals; with tin chloride, a citron-yellow, crystalline compound, $2\text{C}_9\text{H}_8\text{O}, \text{SnCl}_4$, is obtained; the corresponding tin bromide compound melts at 186° . Ethyl cinnamate forms stable compounds, $3\text{C}_{11}\text{H}_{12}\text{O}_2, 2\text{SbCl}_5$; $2\text{C}_{11}\text{H}_{12}\text{O}_2, \text{SnCl}_4$; $\text{C}_{11}\text{H}_{12}\text{O}_2, \text{FeCl}_3$; whilst from cinnamic acid, the compounds $3\text{C}_9\text{H}_8\text{O}_2, 2\text{SbCl}_5$, which forms orange-yellow crystals, $2\text{C}_9\text{H}_8\text{O}_2, \text{SnCl}_4$, faintly red-coloured crystals, and $\text{C}_9\text{H}_8\text{O}_2, \text{FeCl}_3$, bright yellow, hygroscopic needles, are obtained, chloroform being in each case employed as a solvent. Dibenzylideneacetone forms a crystalline compound, $\text{C}_{17}\text{H}_{14}\text{O}, \text{SbCl}_5, \text{HCl}$, and also compounds, $\text{C}_{17}\text{H}_{14}\text{O}, \text{SnCl}_4, \text{HCl}$, large cinnabar-red plates;



blackish-green needles, and $\text{C}_{17}\text{H}_{14}\text{O}, \text{SnBr}_4$, bright red crystals. Cinnamylideneacetophenone forms a blackish-violet, crystalline powder, $\text{C}_{17}\text{H}_{14}\text{O}, \text{SbCl}_5, \text{HCl}$, which dissolves in chloroform giving a deep violet solution with a red lustre. The tin chloride compound,



shows a blue, inky coloration in chloroform and forms a blood-red ethereal solution. The iron compound, $\text{C}_{17}\text{H}_{14}\text{O}, 2\text{FeCl}_3$, separates in black crystals from a deep brown solution. Benzylidenecinnamylideneacetone forms a blackish-green, crystalline powder,

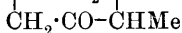


the tin salt, $\text{C}_{19}\text{H}_{16}\text{O}, \text{SnCl}_4, \text{HCl}$, separates in dark blue crystals from the deep red chloroform solution. Dicinnamylideneacetone forms an iron compound, $\text{C}_{21}\text{H}_{18}\text{O}, 2\text{FeCl}_3$, separating from the purplish-red chloroform solution in blackish-green crystals. From these results, the authors draw the conclusion that the tendency of unsaturated compounds containing oxygen to form additive compounds is due to the oxygen, and that the activity of the oxygen is increased by the presence of doubly-linked carbon atoms in the molecule. E. F. A.

Addition of Alkali Hydrogen Sulphites and of Sulphurous Acid to Unsaturated Compounds. EMIL KNOEVENAGEL (*Ber.*, 1904, 37, 4038—4059. Compare Tiemann, *Abstr.*, 1899, i, 247; Harries, this vol., i, 427)—[With ERNST REINECKE].—When shaken with a freshly prepared aqueous solution of sulphur dioxide, dimethylcyclohexenone forms an *additive* compound, which, on evaporation, is obtained as a viscid oil, which gradually becomes yellow. If the aqueous solution is neutralised with sodium carbonate before evapora-

tion, the *sodium* salt, $\text{CH}_2 \begin{smallmatrix} \text{CHMe} \cdot \text{CH}_2 \\ \text{CO} \text{---} \text{CH}_2 \end{smallmatrix} \text{CMe} \cdot \text{SO}_3\text{Na}$, is obtained as a white, crystalline mass. The *additive* compound of 1-methyl-3-phenyl- Δ^3 -cyclohexene-5-one, and sulphurous acid forms the barium salt, $(\text{C}_6\text{H}_5\text{MePh} \cdot \text{SO}_3)_2\text{Ba}$, which crystallises in large prisms.

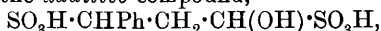
[With ERICH LANGE.]—The *additive* compound, formed on shaking carvone with an 8 per cent. aqueous solution of sulphurous acid, yields the *sodium* salt, $\text{CH}_2 \cdot \text{CMe} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{SO}_3\text{Na}$ (1). This is



obtained on evaporation as a viscid, yellow oil, which solidifies in a desiccator to a yellow, crystalline, hygroscopic mass; it is easily soluble in water or alcohol, but insoluble in ether. The *barium* salt crystallises in monoclinic leaflets.

[With EDMUND SPEYER.]—The *additive* compound obtained from ethyl ethylidenacetate and sulphurous acid forms a *sodium* salt which crystallises in small needles and a crystalline *barium* salt. Benzylidenacetone dissolves only slowly (24 hours) in aqueous sulphurous acid; the *sodium* salt of the *additive* compound is very soluble in water; the *barium* salt and *potassium* salt, $\text{C}_{10}\text{H}_{11}\text{O}_4\text{SK}$, are crystalline; on addition of sodium hydroxide, the *potassium* salt yields benzylidenacetone.

[With R. MORISSE.]—Cinnamaldehyde dissolves in 5 per cent. aqueous sulphurous acid (30 minutes) to a yellow solution; the *additive* compound so formed is decomposed when warmed or on addition of alkali hydroxides or carbonates. The *sodium* salt, formed on addition of sodium acetate, crystallises in glistening leaflets and is identical with the *additive* compound of cinnamaldehyde and sodium hydrogen sulphite; with phenylhydrazine acetate in aqueous solution, it forms the phenylhydrazone of cinnamaldehyde. The action of aqueous sulphurous acid on cinnamaldehyde for 8–10 days leads to the formation of the *additive* compound,



which is more stable than the compound with 1 mol. of sulphurous acid; the *barium* salt, $\text{C}_9\text{H}_{10}\text{O}_7\text{S}_2\text{Ba} \cdot 3\text{H}_2\text{O}$, is crystalline (compare Heusler, Abstr., 1891, 1051). When warmed with dilute sulphuric acid and treated with barium carbonate, the *additive* compound of cinnamaldehyde and 2 mols. of sulphurous acid yield *barium cinnamaldehydesulphonate*, $(\text{COH} \cdot \text{CH}_2 \cdot \text{CHPh} \cdot \text{SO}_3)_2\text{Ba} \cdot 2\text{H}_2\text{O}$, which is hygroscopic. If a freshly prepared aqueous solution of cinnamaldehyde and sulphurous acid is treated with sodium hydroxide, a stable *sodium* salt, $\text{CHPh} \cdot \text{CH} \cdot \text{CH}(\text{OH}) \cdot \text{SO}_3\text{Na}$ (?), is formed, isomeric with Heusler's salt and with cinnamaldehyde sodium hydrogen sulphite.

When shaken with aqueous sulphurous acid for 8–10 hours, phorone forms an *additive* compound with 2 mols. of sulphurous acid; the *sodium* salt is identical with the *additive* compound of phorone and sodium hydrogen sulphite; the *barium* salt, $\text{C}_9\text{H}_{16}\text{O}_7\text{S}_2\text{Ba} \cdot 4\text{H}_2\text{O}$, crystallises in thick needles.

Allylacetone combines with 1 mol. of sulphurous acid; the *sodium* salt and the *barium* salt, $\text{C}_{12}\text{H}_{22}\text{O}_8\text{S}_2\text{Ba} \cdot \text{H}_2\text{O}$, do not yield allylacetone when warmed with aqueous sodium hydroxide, the molecule of sulphurous

acid is therefore probably added to the ethylene linking and not to the carbonyl.

Benzylideneacetophenone does not react with aqueous sulphurous acid; with potassium hydrogen sulphite it forms the *potassium* salt, $C_{15}H_{13}O_4SK$, which crystallises in thick, white needles and yields benzylideneacetophenone when treated with sodium hydroxide or when heated to 155° .

Piperonylideneacetonehydrosulphonic acid, formed when piperonylideneacetone is shaken with aqueous sulphurous acid for 40 hours, is stable in aqueous solution; on concentration, it decomposes to a dark gum-like mass, and on addition of sodium hydroxide yields piperonylideneacetone. The *sodium* salt, $C_{11}H_{11}O_6SNa, 2H_2O$, crystallises in clusters of needles; the *barium* salt, $C_{22}H_{22}O_{12}S_2Ba$, crystallises from dilute alcohol. Piperonylideneacetone dissolves easily in boiling aqueous potassium hydrogen sulphite, forming the *potassium* salt, $C_{11}H_{11}O_6SK, H_2O$.

p-Methoxybenzylideneacetone dissolves in cold aqueous sulphurous acid to a yellow solution which deposits the ketone when warmed on the water-bath; the *sodium* salt, $C_{11}H_{13}O_5SNa, H_2O$, crystallises in small, white needles; the *potassium* salt, $C_{11}H_{13}O_5SK, H_2O$, formed by dissolving the ketone in boiling aqueous potassium hydrogen sulphite, crystallises in small needles.

Cinnamylideneacetone dissolves only slowly in aqueous sulphurous acid (60 hours); the *sulphonic acid* is stable towards alkali carbonates or acids, but is decomposed, with formation of the ketone, on addition of potassium hydroxide. The *barium* salt, $C_{24}H_{26}O_8S_2Ba, 8H_2O$, forms thick crystals and loses $6-7H_2O$ at 100° .

Benzylidenecinnamylideneacetone dissolves only in traces in aqueous sulphurous acid; with aqueous potassium hydrogen sulphite it forms the *potassium* salt of the *bishydrosulphonic acid*, $C_{19}H_{18}O_7S_2K_2, 3H_2O$, which is easily soluble in water and yields the ketone when treated with sodium hydroxide.

Dibenzylideneacetone is insoluble in aqueous sulphurous acid; with aqueous potassium hydrogen sulphite, it forms the *potassium* salt, $C_{17}H_{16}O_7S_2K_2, 3\frac{1}{2}H_2O$, which crystallises in slender needles and yields the ketone when treated with sodium hydroxide or concentrated aqueous potassium carbonate solution.

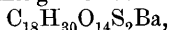
Dipiperonylideneacetone is best prepared by treating piperonal with acetone and concentrated aqueous sodium hydroxide in alcoholic solution; it melts at 185° , is only slightly soluble in aqueous sulphurous acid after 90 hours. The *barium* salt, $C_{19}H_{14}O_{11}S_2Ba$, is obtained by addition of barium carbonate to the solution of the ketone in aqueous sulphurous acid; the *potassium* salt, $C_{19}H_{14}O_{11}S_2K_2, 2\frac{1}{2}H_2O$, is obtained by heating the ketone with aqueous potassium hydrogen sulphite, and yields the ketone when treated with sodium hydroxide.

Dicuminylideneacetone is only slightly soluble in aqueous sulphurous acid; even after shaking for 90 hours, only a very small amount of the *barium* salt, $C_{23}H_{28}O_7S_2Ba, 3H_2O$, is obtained on treatment with barium carbonate. Dicuminylideneacetone reacts with potassium hydrogen sulphite, more slowly than the foregoing ketones, to form the *potassium* salt, $C_{23}H_{28}O_7S_2K_2, 3H_2O$, which yields the ketone on treat-

ment with sodium hydroxide or concentrated aqueous potassium carbonate. The potassium salt, $C_{23}H_{28}O_7S_2K_2, 1\frac{1}{2}H_2O$, was obtained once on recrystallisation from alcohol.

When boiled with aqueous potassium hydrogen sulphite, benzylidene-furfurylideneacetone forms the potassium salt, $C_{15}H_{14}O_8S_2K_2, 2H_2O$, which is decomposed on treatment with sodium hydroxide or aqueous potassium carbonate.

Ethyl ethylidenemalonate dissolves completely in aqueous sulphurous acid; the resulting *hydrosulphonic acid* is stable in aqueous solution, and on evaporation in a vacuum is obtained as a viscid syrup which gradually decomposes, becoming brown. The *barium* salt,



is yellow and deliquesces on exposure to moist air; the *potassium* salt, $C_9H_{15}O_7SK$, is formed by the action of aqueous potassium hydrogen sulphite on the ester.

Ethyl cinnamate is insoluble in aqueous sulphurous acid; with aqueous potassium hydrogen sulphite, it forms the *potassium* salt, $C_{11}H_{13}O_5SK, 1\frac{1}{2}H_2O$, which crystallises in white needles and is hydrolysed to cinnamic acid when boiled with aqueous sodium hydroxide.

Ethyl benzylidenemalonate and potassium hydrogen sulphite, in boiling aqueous solution, form the *potassium* salt, $C_{14}H_{17}O_7SK, 1\frac{1}{2}H_2O$, from which about 15 per cent. of the ester is obtained on treatment with aqueous sodium hydroxide.

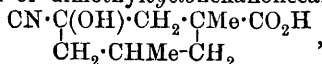
When boiled with aqueous potassium hydrogen sulphite, ethyl cuminyldenemalonate forms the *potassium* salt, $C_{17}H_{23}O_7SK, \frac{1}{2}H_2O$, from which about 18 per cent. of the ester is obtained on treatment with aqueous sodium hydroxide.

G. Y.

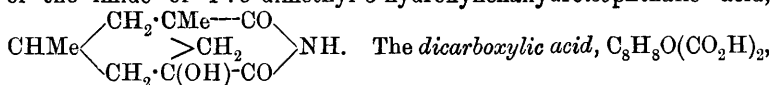
Action of Potassium Cyanide on the Additive Compounds of Alkali Hydrogen Sulphites and Unsaturated Compounds.

EMIL KNOEVENAGEL and ERICH LANGE (*Ber.*, 1904, 37, 4059—4065. Compare foregoing abstract).—When heated with a concentrated aqueous solution of potassium cyanide, sodium 1:3-dimethylcyclohexene-(3)-one-5-hydrosulphonate yields 1-cyano-1:3-dimethylcyclohexane-5-one, $CH_2<\overset{\text{CO}}{\underset{\text{CHMe}}{\text{CH}_2}}>CMe\cdot CN$, which crystallises in plates or long, thin needles, and melts at 92—94°. The *semicarbazone*, $C_{10}H_{16}ON_4$, crystallises in nacreous leaflets and melts at 200—201°. The *carboxylic acid*, $C_6H_7OMe_2\cdot CO_2H$, crystallises with water of crystallisation, sinters at 87°, and melts at 105—120°, or when anhydrous at 124—125°; it is easily soluble in alcohol, ether, warm benzene, or warm water.

Prolonged heating of sodium 1:3-dimethylcyclohexenone with aqueous potassium cyanide leads to the formation of a *substance*, $C_{10}H_{15}O_3N, 2H_2O$, which melts at 204°, loses $2H_2O$ at 210°, and, when anhydrous, crystallises in colourless needles, melts at 220—221°, and is the cyanohydrin of dimethylcyclohexanonecarboxylic acid,



or the imide of 1:5-dimethyl-3-hydroxyhexahydroisophthalic acid,



crystallises from dilute alcohol, and melts at 165—170°, or when anhydrous, at 182—183°. G. Y.

Formation of Additive Compounds of Hydrogen Cyanide and Unsaturated Compounds. EMIL KNOEVENAGEL (*Ber.*, 1904, 37, 4065—4073. Compare foregoing abstracts; Bredt and Kallen, *Abstr.*, 1897, i, 154; Lapworth, *Trans.*, 1903, 83, 999)—[With KARL SCHLEUSSNER].—When boiled with potassium cyanide in aqueous-alcoholic solution, α -phenylcinnamonitrile yields diphenylsuccinonitrile and a substance, $\text{C}_{16}\text{H}_{13}\text{O}_2\text{N}$, which forms white crystals, melts at 196—198°, is soluble in aqueous alkali hydroxides, and is either diphenylsuccinimide or $\alpha\beta$ -diphenyl- β -cyanopropionic acid, as it is hydrolysed to diphenylsuccinic acid by boiling alcoholic potassium hydroxide.

[With P. SCHLÜCHTERER].— α -Phenylcinnamonitrile and hydrogen cyanide, in ethereal solution at the ordinary temperature, formed only traces of diphenylsuccinonitrile in 14 days. The reaction is accelerated by the addition of organic bases, as in 8 days 1 gram of diphenylsuccinonitrile was formed from 5 grams of α -phenylcinnamonitrile and hydrogen cyanide in presence of diethylamine or piperidine in ethereal solution. In presence of ethylamine, 0.8 gram, of amylamine, 0.3 gram, and of quinoline, 0.1 gram of the product was obtained. When heated at 100° for $2\frac{1}{2}$ hours, 5 grams of α -phenylcinnamonitrile and hydrogen cyanide in alcoholic solution formed 1.6 grams of diphenylsuccinonitrile; under the same conditions, but with addition of piperidine, 2.1 grams of product were obtained.

The action of hydrogen cyanide on ethyl benzylideneacetoacetate in presence of piperidine, and hydrolysis of the product leads to the formation of phenylsuccinic acid. The piperidine may be replaced by diethylamine, methylamine hydrochloride, or potassium carbonate.

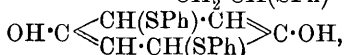
Hydrogen cyanide reacts with benzylideneacetone only in presence of organic bases. The product could not be purified or hydrolysed.

Mesityl oxide and hydrogen cyanide react almost quantitatively in 8 days at the ordinary temperature; the product, on hydrolysis with aqueous potassium hydroxide, yields mesitylic acid.

[With ERICH LANGE].—1:3-Dimethylcyclohexenone, dissolved in concentrated hydrochloric acid, was added to potassium cyanide and water cooled by ice and the mixture left for 5 days. The additive compound formed decomposes on distillation with evolution of hydrogen cyanide and formation of dimethylcyclohexenone; when hydrolysed with aqueous potassium hydroxide, it yields 1:3-dimethylcyclohexanonecarboxylic acid. The oxime, $\text{OH} \cdot \text{N} : \text{C}_6\text{H}_7\text{Me}_2 \cdot \text{CO}_2\text{H}$, forms white crystals and melts at 155—156°; the semicarbazone, $\text{C}_{10}\text{H}_{17}\text{O}_3\text{N}_3$, is a microscopic, crystalline powder and melts at 203—205°. 1:3-Dimethylcyclohexane-5-ol-1:5-dicarboxylic acid, $\text{C}_{10}\text{H}_{16}\text{O}_5$, is formed by the action of hydrogen cyanide on dimethylcyclohexenone; the reaction is accelerated by the addition of organic bases. G. Y.

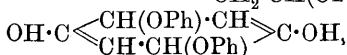
Action of Magnesium Aryl Haloids on Dicarboxylic Acids. WALTHER DILTHEY and E. LAST (*Ber.*, 1904, 37, 3775).—Benzopinacolone, and not β -benzopinacolone (this vol., i, 667), is the product of the action of magnesium phenyl bromide on ethyl oxalate. W. A. D.

Phenoquinone, Thiophenoquinone, and Quinhydrone. THEODOR POSNER (*Annalen*, 1904, 336, 85—167).—Thiophenoquinone (Tröger and Eggert, *Abstr.*, 1896, i, 562) is best represented by the constitutional tautomeric formulæ, $\text{CO} \begin{smallmatrix} \text{CH}(\text{SPh}) \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}(\text{SPh}) \end{smallmatrix} \text{CO}$ and



which agree with its properties and with those of its derivatives. The formation of thiophenoquinone is explained on the basis of Thiele's theory of unsaturated compounds, the phenylmercaptan reacting with the conjugated system $\text{O}:\text{C}:\text{CH}:\text{CH}:$ to form $\text{OH} \cdot \text{C}:\text{CH}:\text{CH}(\text{SPh}) \cdot$.

As thiophenoquinone resembles phenoquinone in its formation, colour, stability, and behaviour on acetylation or benzylation, and in the formation of unstable blue alkali salts, the latter has probably the similar tautomeric constitution: $\text{CO} \begin{smallmatrix} \text{CH}(\text{OPh}) \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}(\text{OPh}) \end{smallmatrix} \text{CO}$ and



which agrees better with its properties than does the constitution suggested by Jackson and Oenslager (*Abstr.*, 1895, i, 513).

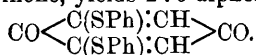
Thiophenoquinone is formed by the action of phenyl mercaptan on a large excess of quinone in light petroleum; if the reaction takes place without a solvent, the mixture becomes black, develops heat, and yields a viscid, blue mass containing quinol and phenyl disulphide.

Thiophenoquinone is moderately stable in indifferent solvents such as benzene or light petroleum, but decomposes when dissolved in hydroxylic solvents such as alcohol or acetic acid; with cold dilute sodium hydroxide, it forms an unstable, dark blue sodium salt which rapidly becomes brown.

3:6-Diphenylthiolquinone, $\text{CO} \begin{smallmatrix} \text{C}(\text{SPh}) \cdot \text{CH} \\ \text{CH} \cdot \text{C}(\text{SPh}) \end{smallmatrix} \text{CO}$, is formed when a solution of thiophenoquinone, in carbon tetrachloride, is shaken with ice and aqueous potassium permanganate. It crystallises in orange-coloured, glistening leaflets, sinters at 252° , melts at 257° , and is insoluble in water, slightly soluble in alcohol or ether, but easily so in boiling glacial acetic acid. It is, in part, completely oxidised on prolonged shaking with an excess of potassium permanganate and sulphuric acid. When reduced with zinc dust in boiling glacial acetic acid solution, it yields 3:6-diphenylthiolquinol, which crystallises in colourless, rectangular plates, melts at 103° , and is easily oxidised to the 3:6-diphenylthiolquinone; the diacetyl derivative, $\text{C}_{22}\text{H}_{18}\text{O}_4\text{S}_2$, crystallises in colourless needles and melts at $168\text{--}168.5^\circ$.

When dissolved in light petroleum, thiophenoquinone gradually decomposes to thiophenol and quinone; the latter oxidises part of the unchanged thiophenoquinone to 3:6-diphenylthiolquinone, itself being reduced to quinol; at the same time, part of the thiopheno-

quinone, by loss and subsequent readdition of 1 mol. of thiophenol, and oxidation by the free quinone, yields 2 : 6-diphenylthiolquinone,

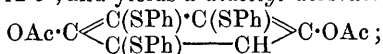


The same reaction takes place, but more quickly, when thiophenoquinone is dissolved in alcohol, but with formation of an additional red substance.

2 : 6-Diphenylthiolquinone crystallises in cherry-coloured needles, melts at 203—204°, and is moderately soluble in boiling alcohol or glacial acetic acid. It is reduced by zinc dust and glacial acetic acid to a greasy product (2 : 6-diphenylthiolquinol?) which, on oxidation with ferric chloride in aqueous alkaline solution, yields 2 : 6-diphenylthiolquinone, and with acetic anhydride forms the *diacetyl* derivative of 2 : 6-diphenylthiolquinol, which melts at 112—114°, and the *diacetyl* derivative of 3 : 6-diphenylthiolquinol.

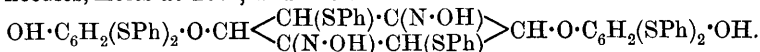
The red substance, $\text{C}_{24}\text{H}_{14}\text{O}_4\text{S}_2$, which is obtained from the reaction of thiophenoquinone with alcohol, forms reddish-brown, glistening crystals, sinters at 85°, melts at 96°, and is easily reduced by zinc dust and acetic acid to a colourless substance; this, when boiled with acetic anhydride, yields the *diacetyl* derivative of 3 : 6-diphenylthiolquinol.

The action of thiophenol on 3 : 6- or 2 : 6-diphenylthiolquinone in boiling glacial acetic acid solution leads to the formation of 2 : 3 : 6-*triphenylthiolquinol*, which separates from alcohol in colourless crystals, melts at 111·5—112·5°, and yields a *diacetyl* derivative,



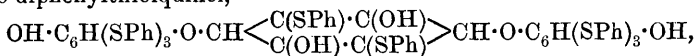
this forms hard, granular crystals and melts at 101—101·5°.

Oxidation of 2 : 3 : 6-triphenylthiolquinol in aqueous alkaline solution by the action of air or of ferric chloride leads to the formation of 2 : 3 : 6-*triphenylthiolquinone*, which crystallises in glistening, reddish-brown scales, melts at 169°, and is reduced to the quinol by zinc dust and glacial acetic acid. The action of hydroxylamine hydrochloride and sodium acetate on 3 : 6-diphenylthiolquinone in glacial acetic acid leads to the formation of 3 : 6-diphenylthiolquinol and of a substance, $\text{C}_{54}\text{H}_{42}\text{O}_6\text{N}_2\text{S}_6$, which crystallises in reddish-brown, glistening needles, melts at 235°, and has the constitution



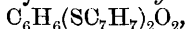
It yields a *tetra-acetyl* derivative which crystallises in brown needles and melts at 163°.

The oxidation of thiophenoquinone by potassium permanganate in presence of an excess of thiophenol leads to the formation of a derivative of 2 mols. of 2 : 3 : 6-diphenylthiolquinol and 1 mol. of 3 : 6-diphenylthiolquinol,



which crystallises in brown leaflets, melts at 164°, and on reduction yields 2 : 3 : 6-triphenylthiolquinol and 3 : 6-diphenylthiolquinol.

[With J. LIPSKI].—When treated with benzyl mercaptan in light petroleum solution, quinone yields *dibenzylthioltetrahydroquinone*,



which crystallises in metallic, glistening needles, melts at 160—163°, and when boiled with acetic anhydride yields quinol. When oxidised by potassium permanganate in ice-cooled light petroleum solution, it yields *dibenzylthiolquinone*, $C_6H_2(SC_7H_7)_2O_2$, which crystallises in dark red leaflets, melts at 223—224°, and is reduced by zinc dust and glacial acetic acid to *dibenzylthiolquinol*, $C_6H_2(SC_7H_7)_2(OH)_2$. This crystallises from dilute alcohol, melts at 134—135°, and yields a *diacetyl* derivative which melts at 203—205°. When the solution of dibenzylthiol-tetrahydroquinone in light petroleum is exposed to light for some weeks, it is converted into dibenzylthiolquinone and a dark blue substance, which sinters at 120°, melts at 136°, and is oxidised by potassium permanganate to a red powder, $C_{26}H_{18}O_4S_2$, melting at 119—121°.

The action of benzyl mercaptan on dibenzylthiolquinone in boiling glacial acetic acid solution leads to the formation of *tribenzylthiolquinol*, $C_6H(SC_7H_7)_3(OH)_2$, which is colourless, melts at 94—98°, and yields dibenzylthiolquinone when oxidised with ferric chloride in alkaline solution, and the *diacetyl* derivative of dibenzylthiolquinol when boiled with acetic anhydride.

Amyl mercaptan and quinone form *diamylthiol-tetrahydroquinone*, which melts at 150—152° and is converted by alcohol or oxidation into *diamylthiolquinone*; this crystallises in red needles and melts at 170—172°. Reduction with zinc dust and acetic acid leads to the formation of *diamylthiolquinol*, which crystallises in colourless needles and melts at 68—70°; the *diacetyl* derivative forms white needles and melts at 103—106°.

Ethyl mercaptan and quinone form a small amount of an additive product; oxidation of the solution leads to *diethylthiolquinone*, which crystallises in red, feathery needles, melts at 159°, and is reduced by zinc dust and acetic acid to *diethylthiolquinol*. This crystallises in needles, melts at 49—50°, and forms a *diacetyl* derivative which melts at 133—134°.

2:5-Toluquinone and phenyl mercaptan in light petroleum form *diphenylthiol-tetrahydrotoluquinone* as a blue precipitate, which melts at 95—97° and after 24 hours has changed into toluquinol and phenyl disulphide.

Diphenylthiol-toluquinone, formed by oxidation by potassium permanganate of a solution of toluquinone and thiophenol in petroleum, crystallises in red needles, melts at 141—142°, and is reduced by zinc dust and acetic acid to *diphenylthiol-toluquinol*, which sinters at 75° and melts at 78—80°; the *diacetyl* derivative crystallises in colourless needles and melts at 121—122°. Toluquinone and benzyl mercaptan, in light petroleum solution, form the additive product, $C_{14}H_{14}O_2S$ or $C_{21}H_{22}O_2S_3$, which melts at 101—103·5°, and on treatment with alcohol or oxidation with potassium permanganate yields *benzylthiol-toluquinone*, $CO < \begin{smallmatrix} CMe=CH \\ CH:C(SC_7H_7) \end{smallmatrix} > CO$, which crystallises in red needles and melts at 136—137°. *Benzylthiol-toluquinol* melts at 113—114·5° and yields a *diacetyl* derivative which crystallises in colourless needles and melts at 120—122°.

When warmed with benzyl mercaptan, benzylthiol-toluquinone

forms *dibenzylthioltoluquinol*, $\text{OH} \cdot \text{C} \begin{smallmatrix} \text{C}(\text{SC}_6\text{H}_5) - \text{CH} \\ \text{CMe} : \text{C}(\text{SC}_6\text{H}_5) \end{smallmatrix} \text{C} \cdot \text{OH}$,

which crystallises in long, colourless needles, sinters at 109° , and melts at 113° ; the *diacetyl* derivative forms colourless needles and melts at $116-117^\circ$. The toluquinol is oxidised by ferric chloride to *dibenzylthioltoluquinone*, which is a brown, amorphous powder and melts at $67-68^\circ$.

Toluquinone reacts with ethyl and with amyl mercaptans in light petroleum solution to form small, dark precipitates which melt at about $102-103^\circ$ and, on oxidation with potassium permanganate, yield oily products.

Xyloquinone and thiophenol do not react in a solvent, but when heated together at 100° yield xyloquinol and phenyl disulphide. Anthraquinone and phenanthraquinone do not react with thiophenol. G. Y.

Introduction of Hydroxyl Groups into Anthraquinone and its Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 153129).—When anthraquinone is dissolved in concentrated sulphuric acid to which mercury or a mercuric salt has been added, and a current of nitrous acid is passed through the warmed solution, a vigorous reaction takes place and the mass becomes brown. The product consists chiefly of 1:4-dihydroxyanthraquinone (quinizarin). The same process may be applied to the derivatives of anthraquinone containing no hydroxyl; thus anthraquinone-2-sulphonic acid yields quinizarinsulphonic acid.

When phosphoric or arsenic acid, or phosphorus oxychloride, is also added to the solution, three hydroxyl groups are introduced, forming purpurin and its derivatives. The purpurinsulphonic acid prepared in this way is more stable than that obtained by direct sulphonation.

Sodium nitrite or nitrososulphuric acid may be employed instead of gaseous nitrous acid. C. H. D.

Preparation of Hydroxy-derivatives of 1-Amino and 1-Alkyl-aminoanthraquinone. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 154353).—When 1-aminoanthraquinone or its methyl or ethyl derivative is dissolved in fuming sulphuric acid (80 per cent.), oxidation takes place in the course of a few days to the corresponding 4-hydroxy-derivative. C. H. D.

Condensation of Anthraquinone with Phenols. WASSILI SCHARWIN, NAUMOF, and SANDURIN (*Ber.*, 1904, 37, 3616—3620. Compare Abstr., 1903, i, 640).—A better yield of phenolanthraquinone than that obtained from anthraquinone, phenol, and stannic chloride by the method previously described is obtained when the operation is conducted in an atmosphere of nitrogen.

Dichlorophenylantraquinone chloride, $\text{CCl}_2 \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C}(\text{C}_6\text{H}_4\text{Cl})_2$, prepared by the action of phosphorus trichloride on diacetylphenol-anthraquinone, separates in colourless prisms and melts at 158.5° . It forms a yellow solution with concentrated sulphuric acid.

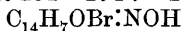
Phenolanthraquinone dimethyl ether, $\text{CO} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C}(\text{C}_6\text{H}_4 \cdot \text{OMe})_2$,

prepared by the Friedel-Crafts reaction from anthraquinone chloride and anisole, separates in yellow rhombohedra, melts at 208° , and forms a reddish-violet solution with concentrated sulphuric acid. Phenolanthraquinone was obtained as a product of its hydrolysis by aluminium chloride. When anthraquinone is condensed with dimethyl-*m*-aminophenol, pyronine is formed. *Pyronine hydrochloride* forms colourless needles and melts and decomposes at 223° . A. McK.

Bromine Derivatives of Phenanthraquinone. JULIUS SCHMIDT (*Ber.*, 1904, 37, 3551—3556).—A theoretical introduction to the following communications. G. Y.

The Phenanthrene Series. XI. Phenanthraquinone Dibromide. JULIUS SCHMIDT and ERHARD JUNGHaus (*Ber.*, 1904, 37, 3556—3558).—The action of bromine on phenanthraquinone mixed with a small quantity of water and cooled by ice leads to the formation of *phenanthraquinone dibromide*, $\text{C}_{14}\text{H}_8\text{O}_2\text{Br}_2$, which is obtained as a reddish-brown mass. It rapidly decomposes with loss of bromine, and, when boiled with water, yields phenanthraquinone and 2-bromophenanthraquinone. G. Y.

The Phenanthrene Series. XII. 2-Bromophenanthraquinone and its Derivatives. JULIUS SCHMIDT and ERHARD JUNGHaus (*Ber.*, 1904, 37, 3558—3567).—*2-Bromophenanthraquinone*, $\text{C}_{14}\text{H}_7\text{O}_2\text{Br}$, prepared by heating phenanthraquinone with bromine in aqueous solution in a sealed tube at 100° , crystallises from glacial acetic acid in glistening, yellowish-red needles and leaflets, melts at $233\text{—}234^\circ$, dissolves in concentrated sulphuric acid to a green solution, which becomes reddish-brown when warmed, and, on further treatment with bromine, yields 2:7-dibromophenanthraquinone. 2-Bromophenanthraquinone (bromodiphenylenequinoxaline), $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N}:\text{C}\cdot\text{C}_6\text{H}_4 \\ \text{N}:\text{C}\cdot\text{C}_6\text{H}_3\text{Br} \end{smallmatrix}$, obtained when 2-bromophenanthraquinone is boiled with *o*-phenylenediamine hydrochloride in alcoholic solution, crystallises in sheaves of brown needles and melts at $252\text{—}254^\circ$. The *monoxime*,



(*Abstr.*, 1902, i, 797), crystallises in orange-coloured, matted needles and melts at $163\text{—}164^\circ$. The *monophenylhydrazone*, $\text{C}_{14}\text{H}_7\text{OBr}\cdot\text{N}_2\text{HPh}$, is formed by the action of phenylhydrazine hydrochloride on 2-bromophenanthraquinone in alcoholic solution; it crystallises in red needles and melts at $171\text{—}172^\circ$. The action of phenylhydrazine on 2-bromophenanthraquinone results in the reduction of the quinone to 2-bromo-8:9-dihydroxyphenanthrene, which is unstable. The *diacetyl* derivative obtained by boiling the reduction product with acetic anhydride crystallises in sheaves of white needles and melts at $178\text{—}179^\circ$. The *monoimide*, $\text{C}_6\text{H}_3\text{Br}\cdot\text{C}(\text{NH})\text{CO}$ (?), obtained by the action of alcoholic ammonia on 2-bromophenanthraquinone, crystallises in

glistening, golden needles, melts and decomposes at 169° , and dissolves in alcohol to a yellow solution which becomes green when boiled. The action of alcoholic ammonia on 2-bromophenanthraquinone at $130-140^{\circ}$ leads to the formation of *dibromophenanthrazine*,

$$\begin{array}{c} \text{C}_6\text{H}_5\text{Br} \cdot \text{C} \cdot \text{N} \cdot \text{C} \cdot \text{C}_6\text{H}_5\text{Br} \\ | \quad | \quad | \\ \text{C}_6\text{H}_4 - \text{C} \cdot \text{N} \cdot \text{C} \cdot \text{C}_6\text{H}_4 \end{array}$$

or
$$\begin{array}{c} \text{C}_6\text{H}_5\text{Br} \cdot \text{C} \cdot \text{N} \cdot \text{C} \cdot \text{C}_6\text{H}_4 \\ | \quad | \quad | \\ \text{C}_6\text{H}_4 - \text{C} \cdot \text{N} \cdot \text{C} \cdot \text{C}_6\text{H}_5\text{Br} \end{array}$$
, which crystallises in glistening, brown needles, does not melt at 350° , and sublimes without decomposition when strongly heated.

When heated at 100° with sulphuric acid containing 4 per cent. of sulphur trioxide, 2-bromophenanthraquinone yields a monosulphonic acid containing a small amount of disulphonic acid; with sulphuric acid containing 35 per cent. of sulphur trioxide at the ordinary temperature, it yields almost wholly the disulphonic acid.

2-Bromophenanthraquinonesulphonic acid, $\text{C}_{14}\text{H}_6\text{O}_2\text{Br} \cdot \text{SO}_3\text{H}$, forms a brownish-red, crystalline mass, is easily soluble in water, but insoluble in anhydrous organic solvents, forms *salts* which are easily soluble in water, and in aqueous solution colours wool-brown. 2-Bromophenanthraquinonedisulphonic acid, $\text{C}_{14}\text{H}_6\text{O}_2\text{Br}(\text{SO}_3\text{H})_2$, resembles, but is more hygroscopic and darker coloured than, the monosulphonic acid. 2-Bromophenanthraquinone is oxidised by potassium dichromate and sulphuric acid to *p-bromodiphenic acid*, $\text{C}_6\text{H}_4(\text{CO}_2\text{H}) \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{CO}_2\text{H}$, which crystallises in white leaflets, melts at $238-239^{\circ}$, and forms a *silver salt* which crystallises in white needles. G. Y.

The Phenanthrene Series. XIII. 2:7-Dibromophenanthraquinone and its Derivatives. JULIUS SCHMIDT and ERHARD JUNGHAUS (*Ber.*, 1904, 37, 3567—3570).—2:7-Dibromophenanthraquinone, obtained by bromination of phenanthraquinone or of 2-bromophenanthraquinone at $150-160^{\circ}$, forms reddish-yellow needles and melts at 323° . It is also formed in small amount by the action of cuprous bromide on the diazo-solution obtained from 2:7-diaminophenanthraquinone (this vol., i, 70). 2:7-Dibromophenanthraquinone is oxidised by potassium dichromate and sulphuric acid to 4:4'-*dibromodiphenic acid*, which is also formed by the action of cuprous bromide on diazotised 4:4'-diaminophenic acid. It crystallises in white needles and melts at $277-278^{\circ}$.

2:7-Dibromophenanthraphenazine,
$$\begin{array}{c} \text{C}_6\text{H}_3\text{Br} \cdot \text{C} \cdot \text{N} \\ | \quad | \\ \text{C}_6\text{H}_3\text{Br} \cdot \text{C} \cdot \text{N} \end{array} > \text{C}_6\text{H}_4$$
, crystallises in green needles and melts at $294-295^{\circ}$. 2:7-Dibromophenanthraquinone monoxime, $\text{C}_{14}\text{H}_7\text{O}_2\text{Br}_2\text{N}$, forms red needles and melts and decomposes at $229-230^{\circ}$. The *monoimide*, $\text{C}_{14}\text{H}_7\text{Br}_2\text{ON}$, crystallises in long, red needles and melts and decomposes at $231-232^{\circ}$. Tetra-bromophenanthrazine, $\text{C}_{28}\text{H}_{12}\text{N}_2\text{Br}_4$, formed from 2:7-dibromophenanthraquinone, crystallises in microscopic needles and does not melt at 350° . G. Y.

The Phenanthrene Series. XIV. 3-Bromophenanthraquinone and its Derivatives. JULIUS SCHMIDT and GUSTAV LADNER (*Ber.*, 1904, 37, 3571—3572).—3-Bromophenanthraquinone,

obtained by oxidation of 3:9-(or 3:10-)dibromophenanthrene, crystallises in glistening, yellow needles, melts at 268° , and dissolves in cold concentrated sulphuric acid to a dark brown solution. It is oxidised by potassium dichromate and sulphuric acid to 5-bromodiphenic acid, which crystallises in white needles, melts and decomposes at 257° , and is converted by potassium permanganate in sulphuric acid solution into *p*-bromobenzoic acid.

3-Bromophenanthraquinone monooxime crystallises in slender, yellow needles and melts at 198° . 3-Bromophenanthraphenazine crystallises in yellow needles and melts at 249° . G. Y.

The Phenanthrene Series. XV. Bromo- and Bromonitro-derivatives of Phenanthrene. JULIUS SCHMIDT and GUSTAV LADNER (*Ber.*, 1904, 37, 3573—3577).—9-Bromo-10-nitrophenanthrene, obtained by warming 9-bromophenanthrene with concentrated nitric acid (Werner, *Abstr.*, 1902, i, 440), or better by the action of nitrogen peroxide on an ice-cold solution of 9-bromophenanthrene in benzene, is reduced by stannous chloride and hydrochloric acid in boiling glacial acetic acid solution to 10-aminophenanthrene (*Abstr.*, 1903, i, 691).

When heated with bromine and water in a sealed tube at 100° , 10-nitrophenanthrene forms a dibromide, $C_{14}H_9O_2Br_2N$, which crystallises in glistening, yellow leaflets, melts at 81 – 82° , and is not oxidised when warmed with chromic acid in glacial acetic acid solution.

The action of bromine on phenanthrene in boiling chloroform solution leads to the formation of 3:9-(or 3:10-)dibromophenanthrene (see foregoing abstract), which melts at 146° (Werner, *loc. cit.*).

G. Y.

Preparation of Solid Camphene. CHEMISCHE FABRIK AUF AKTIEN VORM E. SCHERING (D.R.-P. 154107. Compare this vol., i, 680).—Solid camphene, free from chlorine, is obtained on heating, under pressure, pinene hydrochloride, hydrobromide, or hydriodide with aqueous solutions of piperidine, or of the fatty bases, such as methylamine, dimethylamine, diamylamine, or piperazine. C. H. D.

Terpenes and Ethereal Oils. LXIX. Phellandrene. OTTO WALLACH [with ERICH BESCHKE] (*Annalen*, 1904, 336, 9—46. Compare *Abstr.*, 1887, 967; 1888, 1204; 1891, 1084; 1896, i, 101; 1901, i, 89; 1903, i, 105).—*d*-Phellandrene, obtained from elemi oil, is chemically and physically identical with *d*-phellandrene from bitter-fennel oil, but not with *d*-phellandrene from water-fennel oil. The former is to be called *d*- α -, the latter *d*- β -phellandrene. *l*-Phellandrene, from eucalyptus oil, is *l*- α -phellandrene. *d*- α -Phellandrene is now found to boil at 61° under 11 mm. pressure and to have a sp. gr. 0.844 at 19° , and n_D^{20} 1.4732.

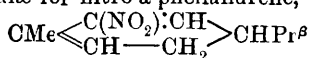
The two nitrites formed from α -phellandrene (Schreiner, *Abstr.*, 1901, i, 600) are separated by recrystallisation from acetone and alcohol. *d*- α -Phellandrene α -nitrite melts at 112 – 113° and has $[\alpha]_D - 138.4^{\circ}$; *l*- α -phellandrene α -nitrite melts at 112 – 113° and has $[\alpha]_D + 135.93^{\circ}$ to $+142.6^{\circ}$. *d*- α -Phellandrene β -nitrite melts at 105° and has $[\alpha]_D + 45.8^{\circ}$; *l*- α -phellandrene β -nitrite melts at 105° and has

$[\alpha]_D - 40.287^\circ$ to -40.817° . The α - and β -nitrites of α -phellandrene are chemically identical. Contrary to Semmler's statement (Abstr., 1903, i, 641), they are only slowly oxidised by potassium permanganate in acetone solution. When acted on by nitric acid in glacial acetic acid solution, they yield *trinitro-p-cymene*, $C_{10}H_{15}O_6N_3$, which crystallises in yellow prisms, melts at $136-137^\circ$ (Abstr., 1901, i, 89), and has $[\alpha]_D + 191.0^\circ$ to $+195.92^\circ$ when prepared from the nitrites of *l*- α -phellandrene, -188.13° to -188.30° when prepared from the nitrites of *d*- α -phellandrene. When reduced with zinc and hydrochloric acid, it yields 2:5-diamino-*p*-cymene dihydrochloride. When warmed with fuming hydrochloric acid at 60° , α -phellandrene nitrite yields *p*-cymene, a small amount of a *ketone*, which boils above 200° under the ordinary pressure, dichlorothymoquinone (Andreson, *J. pr. Chem.*, 1881, [ii], 23, 176), which melts at 99° , and chlorothymoquinone (Kehrmann, Abstr., 1900, i, 180), which forms a *semicarbazone*, $C_{11}H_{14}O_2N_3Cl$, melting at 230° . When warmed with tin and hydrochloric acid until the yellow colour disappears, dichlorothymoquinone yields *chlorothymoquinol*, $C_{10}H_{13}O_2Cl$, which melts at 70° ; if the heating with tin and hydrochloric acid is prolonged, the product is thymoquinol.

The action of sulphuric acid (3 of acid : 2 of water) on α -phellandrene nitrite leads to the formation of (1) *p*-cymene; (2) a *ketone* which boils at $110-114^\circ$ under 16 mm. pressure and forms an *oxime*, $C_{10}H_{17}ON(?)$, melting at $87-88^\circ$; (3) *hydroxythymoquinone*, $C_{10}H_{12}O_3$, which forms red crystals, melts at 170° , boils at $125-134^\circ$ under 16 mm. pressure, and yields a *semicarbazone*, $C_{11}H_{15}O_3N_3$, melting at $214-217^\circ$, and (4) thymoquinone.

Nitro- α -phellandrene, obtained from α -phellandrene nitrite, is isomeric with Pesci's nitrophellandrene (Abstr., 1896, i, 101), which was formed from β -phellandrene nitrite, and has $[\alpha]_D$ approximately the same as for the nitrite from which it is obtained. When reduced with zinc dust in acetic acid solution, nitro- α -phellandrene yields *l*-carvotanacetone ($\Delta^{5,6}$ -methene-2-one), its *oxime*, and a small amount of a base (dihydrocarvacrylamine?). *l*-Carvotanacetone boils at $227-229^\circ$, has an intense odour of carvone, a sp. gr. 0.9345, $n_D 1.4822$ at 19° , and, with hydrogen sulphide in alcoholic ammoniacal solutions, forms an additive compound which crystallises in needles and melts at 220° . The *oxime*, $C_{10}H_{16}NOH$, crystallises in prisms and melts at $75-76^\circ$; the *oxime* derived from *l*- α -phellandrene has $[\alpha]_D - 19.155^\circ$, that from *d*- α -phellandrene has $[\alpha]_D + 19.20^\circ$; on crystallisation of a molecular mixture of the *l*- α - and *d*- α -rotatory *oximes*, the racemic modification melting at $92-93^\circ$ is obtained. The *semicarbazone* crystallises in needles which change into transparent prisms, melts at 173° , and has $[\alpha]_D - 112.40^\circ$ to -113.79° if obtained from *l*- α -phellandrene, $[\alpha]_D + 114.69^\circ$ if from *d*- α -phellandrene; the racemic modification obtained by crystallising a molecular mixture of the *d*- α - and *l*- α -rotatory modifications melts at $177-178^\circ$ (compare Semmler, Abstr., 1900, i, 676; Harries, Abstr., 1901, i 551).

From the constitution of carvotanacetone are to be derived the constitutional formulæ for nitro- α -phellandrene,



for α -phellandrene nitrite, $\text{CMe} \begin{array}{c} \text{CH(NO}_2\text{)} \cdot \text{CH(NO)} \\ \text{CH} \text{---} \text{CH}_2 \end{array} \text{CHPr}^\beta$, and
for α -phellandrene, $\text{CMe} \begin{array}{c} \text{CH=CH} \\ \text{CH} \cdot \text{CH}_2 \end{array} \text{CHPr}^\beta$.

d - β -Phellandrene boils at 57° under 11 mm. pressure and has a sp. gr. 0.8520, n_D 1.4788 at 20° , and $[\alpha]_D + 18.54^\circ$. The nitrite melts at 98° (see Abstr., 1903, i, 105) and on recrystallisation from acetone yields an α -modification, which melts at 102° and has $[\alpha]_D - 159.3^\circ$, and a β -modification, which melts at 97 – 98° and in 8.5 per cent. solution shows no optical activity.

When reduced with zinc dust and acetic acid, nitro- β -phellandrene yields chiefly a diamine (Abstr., 1903, i, 105) and a small amount of a ketone which boils at 111 – 112° under 13 mm. pressure, and has a characteristic odour resembling neither carvone nor menthone; the semicarbazone crystallises in white needles, becomes yellow on exposure to light, and melts at 200 – 202° ; the oxime melts at 42 – 44° and boils at 150° under 12 mm. pressure. G. Y.

Matico Oil and Matico-camphor. HERMANN THOMS (*Chem. Centr.*, 1904, ii, 1125; from *Apoth.-Zeit.*, 19, 771–773).—The composition of a sample of matico oil obtained by Schimmel & Co. from leaves of *Piper angustifolium*, received in April, 1904, has been found to be quite different from that examined previously. It contained 10 per cent. of asarone, together with cineol, a mixture of terpenes, and a hydrocarbon, but, unlike the earlier sample, neither dill-apiole nor parsley-apiole. Matico-camphor, $\text{C}_{15}\text{H}_{26}\text{O}$, melts at 94° and has $[\alpha]_D - 28.73^\circ$. The camphor is a sesquiterpene alcohol, since on boiling with a 50 per cent. solution of sulphuric acid it forms a sesquiterpene with elimination of water. E. W. W.

Oleum Pini Sylvestris and Oleum Pini Strobi. JULIUS TRÖGER and ALFRED BEUTIN (*Arch. Pharm.*, 1904, 242, 521–532).—Two samples of oil were examined, obtained from young twigs gathered in the spring. One was obtained from *Pinus sylvestris*, grown in Germany, and had a sp. gr. 0.871 at 20° ; it contained 3.23 per cent. of esters (reckoned as bornyl acetate) and 9.3 per cent. of alcohols (reckoned as bornyl alcohol). d -Pinene was present in quantity, but neither sylvestrene nor cadinene could be detected, although these are present in needles gathered in the winter (Bertram and Walbaum, Abstr., 1893, i, 660).

The second sample was purchased in Germany, but was called "Weymouth pine oil"; it had sp. gr. 0.901 at 15° , n_D 1.4827 at 20° , and $\alpha_D - 39.70^\circ$ in a 200 mm. tube, and it contained 8.6 per cent. of esters and 5.2 per cent. of alcohols (calculation as before). d -Pinene was present in quantity, but no other substance could be isolated with certainty. C. F. B.

Copaiva Balsam from Surinam. LEOPOLD VAN ITALLIE and C. H. NIEUWLAND (*Arch. Pharm.*, 1904, 242, 539–546).—Some samples were examined which had been collected in Surinam from *Copaifera guianensis*, and found by J. F. Pool to contain 78 per cent.

of essential oil when fresh; the acid number was 34, the iodine number 94; esters were not present. The *essential oil* was obtained by distillation with water, had a sp. gr. 0.91 and boiled between 250° and 260°; from a solution of the residual resin in alcohol, a crystalline *copaivic acid* melting at 130° had been isolated. The bulk of the oil boiled at 254—262° and seemed to be a mixture of two *sesquiterpenes*. From the fraction boiling at 270—280°, a little cadinene dihydrochloride was prepared by diluting the fraction with ether and passing hydrogen chloride in. Towards the end of the distillation of the balsam with steam, a crystalline *sesquiterpene alcohol*, $C_{15}H_{26}O$ (molecular weight determined), melting at 113—115°, separated in the condenser; this gave the reactions of a cholesterol, but seemed not to form an acetate when warmed with acetic anhydride in pyridine solution. C. F. B.

Constituents of White Peru Balsam. HERMANN THOMS and A. BILTZ (*Chem. Centr.*, 1904, ii, 1047; from *Zeit. Oesterr. Apoth.-V.*, 42, 943—947. Compare Abstr., 1902, i, 634).—The following substances have been isolated from white Peru balsam: (1) myroxocerin (compare Germann, Abstr., 1897, ii, 185), a white, amorphous substance, which melts at 120—130°, and is soluble in benzene, ethyl acetate, or chloroform, but insoluble in absolute alcohol or alkalis. (2) A compound which crystallises from dilute alcohol in needles, melts and decomposes at 270°, and is soluble in a 5 per cent. solution of sodium carbonate. This substance does not contain nitrogen. (3) Cinnamic acid. (4) A brownish-yellow substance which may be extracted by means of a 1 per cent. solution of potassium hydroxide and softens at 100° (myroxol). By the action of an alcoholic solution of potassium hydroxide on the balsam, cinnamic acid, cinnamyl alcohol, and phenylpropyl alcohol are formed. The balsam probably also contains a hydrocarbon which has the odour of cedar wood. The presence of benzyl alcohol and peruvial was not detected. E. W. W.

Galbanic Acid. ALEXANDER TSCHIRCH and K. G. v. KÜYLENSTJERNA (*Arch. Pharm.*, 1904, 242, 533—537).—A sample of this acid sent by Hirschsohn (compare Tschirch and Knitl, Abstr., 1899, i, 714) has been examined. It melts at 155—156° and has the composition $C_{13}H_{20}O_2$. If this is the molecular formula (molecular weight determinations gave uncertain results), the acid is monobasic; the *silver* and *barium* salts were analysed; the acid number is about 11 per cent. less than the theoretical, and the saponification number is little greater; the iodine number is about 8 per cent. less than corresponds with the presence of one ethylene linking; an acetyl derivative could not be prepared. C. F. B.

Caoutchouc. Latex from Sicily. CARL D. HARRIES (*Ber.*, 1904, 37, 3842—3848. Compare Weber, Abstr., 1903, i, 845; de Jong and de Haas, this vol., ii, 762, 763).—The fresh juice of *Ficus magnolioides* has been examined. When extracted with ether and the ethereal solution filtered and evaporated, an oil is obtained consisting of a mix-

ture of an oxygen compound, $C_{30}H_{48}O_3$, and an elastic substance of the same composition as paracaoutchouc (Abstr., 1902, i, 811). It also yields the same nitrosite. The oxygen compound begins to crystallise when the oil is kept, but the two compounds are most readily separated by solution in ether and precipitation with alcohol, in which the elastic mass is insoluble. Its solubility in ether also diminishes as the oxygen compound is removed. It also becomes less soluble after repeated treatment with formic acid.

The oxygen compound crystallises from alcohol in colourless plates, melts at 115° after sintering at 111° , and occurs in large quantity in the extract. *Ficus elastica* yields an oxygen compound, $C_{20}H_{32}O_2$, which sinters at 185° and melts at 195° . This is mixed with about an equal quantity of the elastic substance in the original extract.

J. J. S.

Caper-rutin. D. H. BRAUNS (*Arch. Pharm.*, 1904, 242, 556—560. Compare this vol., i, 681).—Caper-rutin was isolated from caper buds that had been preserved in vinegar, by extraction with boiling water; from dried buds that had already opened, no rutin could be obtained. Caper-rutin is identical in properties and reactions with the rutin of rue (Waliaschko, this vol., i, 760) and with sophorin (following abstract); each of these substances yields rhamnose and dextrose on hydrolysis with dilute sulphuric acid, in addition to a product, $C_{15}H_{10}O_7$ (quercetin, sophoretin), which in all three cases exhibits the same properties and reactions.

C. F. B.

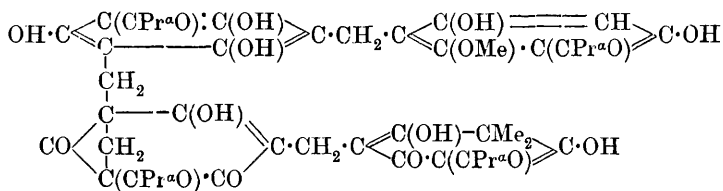
Sophorin. D. H. BRAUNS (*Arch. Pharm.*, 1904, 242, 547—556. Compare this vol., i, 681).—Sophorin, $C_{27}H_{30}O_{16}$, was extracted from Chinese yellow-berries by boiling the drug, which consisted of flower buds, flower stalks, and stems, with water, and allowing the extract to cool, when the glucoside crystallised out; the yield of the crude substance was 27 per cent. When dried in the air, it contains nearly $3H_2O$; when dried over sulphuric acid, under diminished pressure, it retains $2H_2O$, and then takes up the additional H_2O when exposed to the air; it does not do this after it has been dried at 110° , when it loses all its water. The sophoretin, $C_{15}H_{10}O_7$, obtained by hydrolysing sophorin with dilute sulphuric acid, melts at 297 — 300° , and crystallises with $2H_2O$, which are lost at 100° , and slowly at the ordinary temperature under diminished pressure; in the latter case, they are taken up again in the air, not so when the drying has been effected at 100° . In these respects, and also in respect of its acetyl derivative, sophoretin is identical with quercetin. Rhamnose and dextrose were also identified as products of the hydrolysis of sophorin, which takes place in accordance with the equation $C_{27}H_{30}O_{16} + 3H_2O = C_{15}H_{10}O_7 + C_6H_{14}O_6 + C_6H_{12}O_6$; evidently sophorin is identical with rutin from rue (Waliaschko, this vol., i, 760).

C. F. B.

Filmarone, the Anthelmintic Substance in Filix Extract. FRIEDRICH KRAFT (*Arch. Pharm.*, 1904, 242, 489—500. Compare Abstr., 1902, i, 814, and Boehm, Abstr., 1898, i, 40; 1899, i, 32, 804; 1902, i, 36, &c.; this vol., i, 403, 406, &c.).—The substance

previously described by the author as flavaspidin is probably identical with Boehm's phloraspin (this vol., i, 409).

The amorphous acid previously described, which forms the chief component of the extract, is now named *filmarone*. When heated for 8 hours with zinc dust and 15 per cent. aqueous sodium hydroxide, it yields fillic acid, a substance melting at 137°, filicyl-*n*-butanone (Boehm, Abstr., 1902, i, 36), methylphloroglucinyl methyl ether, melting at 118—119°, phloroglucinol, and trimethylphloroglucinol, with some methyl- and dimethyl-phloroglucinols and butyric acid. If the boiling is continued for 5 minutes only, merely traces of fillic acid are obtained and more of the substance melting at 137°. This was identified with aspidinol or methylphloroglucinylbutanone methyl ether (Boehm, Abstr., 1902, i, 37). After repeated recrystallisation, it melted at 155—158°. With diazoaminobenzene in alcoholic solution, filmarone yields benzenedisazophloroglucinyl-*n*-butanone (Boehm, Abstr., 1902, i, 39); in carbon tetrachloride solution, benzeneazomethylphloroglucinyl-*n*-butanone (*ibid.*, 38) is obtained. In consequence of these decompositions, the formula given below, equal to $C_{47}H_{54}O_{16}$, is assigned to filmarone; it is supported by the ascertained percentages of carbon and hydrogen, of methoxyl and of butyric acid, and by the percentage of calcium in the *calcium* salt (filmarone functions as a dibasic acid).



Filmarone.

C. F. B.

Theory of Dyeing. RICHARD WILLSTÄTTER (*Ber.*, 1904, 37, 3758—3760).—If, in dyeing, the dye combines chemically with the fibre, it might be possible by such a process to resolve a racemic substance which is absorbed by the fibre into its antipodes. Experiments were made from this standpoint with the inactive alkaloids atropine, homatropine, and tropacocaine, which are absorbed from their solutions in considerable quantity by wool; in all cases, however, both the alkaloid absorbed by the wool and that left behind in solution were equally inactive.

W. A. D.

Transformation of True Colour Bases into Carbinol Bases and of True Cyanide Dyes into Leuco-cyanides. PAUL GERLINGER (*Ber.*, 1904, 37, 3958—3963).—The transformation of a true colour base into the corresponding carbinol and of a true cyanide dye into a leuco-cyanide is a reaction of the second order. The following transformations were studied: brilliant-green base at 0°, crystal-violet base at 0° and at 25°, pararosaniline base at 0° and at 25°, pararosaniline cyanide at 25°, and auramine base at 25°.

A. McK.

Melanic Pigments. MARUSSIA BAKUNIN and G. DRAGOTTI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1904, [iii], 10, 222—240).—The pigment investigated by the author was isolated from melanotic nodules by means of sodium carbonate solution, which converted it into a soluble compound, probably the sodium salt. The pigment was then reprecipitated by hydrochloric acid.

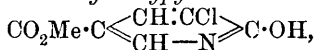
The material thus obtained consists of a mixture of at least two different substances: (1) dull brown melanin, which does not give concordant numbers on analysis, and (2) shining black *melanin*, to which the formula $C_{39}H_{58}O_{15}N_6S$ is given. The latter yields with aqueous ammonia a *hydroxide* of the formula $C_{39}H_{56}O_{15}N_6S(OH)_2$, and also forms a *silver* salt, $C_{39}H_{56}O_{15}N_6SAg_2$.

The brown, dull melanin, when treated with an alcoholic solution of piperidine and the liquid precipitated with hydrochloric acid, yields a black *pigment*, $C_{60}H_{89}O_{18}N_6S$, which is slightly soluble in acetic acid and readily in ammonia or sodium hydroxide solution; it gives a *silver* salt, $C_{60}H_{84}O_{18}N_6SAg_5$. T. H. P.

Chlorocoumalinic Acid and its Conversion into Pyridine Derivatives. HANS VON PECHMANN and WILLIAM H. MILLS (*Ber.*, 1904, 37, 3829—3836. Compare Feist, *Abstr.*, 1901, i, 557).—The *chlorocoumalinic acid* obtained by the action of chlorine in an acetic acid solution of coumalinic acid in the presence of iodine has the

constitution $CO_2H \cdot C \begin{smallmatrix} \text{CH} : CCl \\ \text{CH} - O \end{smallmatrix} > CO$, since it can be converted into 3-chloropyridine. It forms compact crystals from acetic acid, melts at 187—189°, and is sparingly soluble in chloroform or benzene. It dissolves in sodium carbonate solution and can be precipitated unaltered on the addition of acid; both sodium hydroxide and boiling water decompose it.

The *methyl* ester, obtained by esterifying the acid, or even better by chlorinating methyl coumalinate, crystallises in colourless, thick prisms and melts at 134—136°. It is decomposed when boiled with water, is insoluble in sodium carbonate solution, but dissolves in the corresponding hydroxide. Concentrated ammonia converts the methyl ester into *methyl 3-chloro-2-hydroxypyridine-5-carboxylate*,



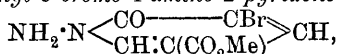
which crystallises from water in prismatic needles melting at 218°. It possesses acidic properties, and crystalline *sodium* and *barium* derivatives have been prepared. The free *acid* crystallises in plates, melts and decomposes at 308°, and is only sparingly soluble in the usual organic solvents. The majority of its salts are sparingly soluble.

2:3-Dichloropyridine-5-carboxylic acid, obtained by the action of phosphorus oxy- and penta-chlorides on the hydroxy-acid, crystallises from dilute alcohol with $1H_2O$, melts at 162—163°, and yields a characteristic *lead* salt which forms feathery crystals. When the acid is heated, it loses hydrogen chloride and yields a product from which chloropyridonecarboxylic acid has been obtained.

The dichloro-acid, on reduction with hydriodic acid, potassium iodide, and red phosphorus, yields 3-chloropyridine-5-carboxylic acid, which melts at

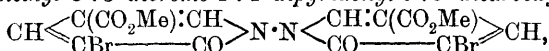
170—171° and is very sparingly soluble in benzene. Its silver salt, when heated, yields chloronicotinic acid and 3-chloropyridine, which is extremely stable towards sodic methoxide (compare Lieben and Haitinger, Abstr., 1885, 966). J. J. S.

Action of Hydrazine Hydrate on Methyl Bromocoumalinate. HANS VON PECHMANN and WILLIAM H. MILLS (*Ber.*, 1904, 37, 3836—3841).—*Methyl 3-bromo-1-amino-2-pyridone-5-carboxylate*,



is obtained by the action of a 50 per cent. solution of hydrazine hydrate on methyl bromocoumalinate. It may be separated from unaltered coumalinate by solution in hydrochloric acid, crystallises from benzene or hot water, and melts at 144—145.5°. It is only feebly basic, and solutions of its salts precipitate the base on the addition of much water. It readily condenses with benzaldehyde, yielding a *hydrazone*, $\text{C}_7\text{H}_5\text{O}_3\text{Br} \cdot \text{N} \cdot \text{N} : \text{CHPh}$, which crystallises in minute, colourless needles melting at 173°, and on treatment with nitrous acid yields methyl bromohydroxynicotinate and nitrous oxide.

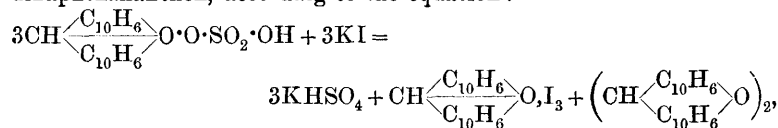
3-Bromo-1-amino-2-pyridone-5-carboxylic acid, obtained by hydrolysing the ester with methyl alcoholic sodium hydroxide, melts at 238° and its aqueous solution has a sweet taste and reduces Fehling's solution on boiling. It condenses with benzaldehyde, yielding *benzylideneaminobromopyridonecarboxylic acid*, $\text{C}_{13}\text{H}_9\text{O}_3\text{N}_2\text{Br}$, which melts at 243°. The methyl ester reacts with methyl bromocoumalinate yielding *methyl 3 : 3'-dibromo-1 : 1'-dipyridonyl-5 : 5'-dicarboxylate*,



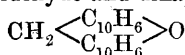
which crystallises from nitrobenzene in small prisms melting at 344°, and is sparingly soluble in all ordinary solvents. On reduction, it yields methyl bromopyridonecarboxylic acid. J. J. S.

An Organic Persulphate. ROBERT FOSSE and P. BERTRAND (*Compt. rend.*, 1904, 139, 600—602. Compare this vol., i, 816).—

Dinaphthaxanthonium sulphate, $\text{CH} \begin{array}{c} \text{C}_{10}\text{H}_6 \\ \text{C}_{10}\text{H}_6 \end{array} \text{O} \cdot \text{O} \cdot \text{SO}_2 \cdot \text{OH}$, obtained by the action of dilute sulphuric acid on dinaphthaxanthidrol or on bis-dinaphthaxanthen oxide, forms red crystals containing 1 mol. of sulphuric acid and varying proportions of water according to the strength of the acid employed in the preparation; it reacts with potassium iodide to form dinaphthaxanthen tri-iodide (di-iododinaphthaxanthonium iodide? Compare Abstr., 1902, i, 304, 689) and bis-dinaphthaxanthen, according to the equation:



and with alcohol to form aldehyde and dinaphthaxanthen,



(*loc. cit.*), and is therefore to be regarded as a derivative of Caro's monopersulphuric acid, $\text{H}\cdot\text{O}\cdot\text{O}\cdot\text{SO}_2\cdot\text{OH}$. M. A. W.

Pyrone. RICHARD WILLSTÄTTER and RUDOLF PUMMERER (*Ber.*, 1904, 37, 3740—3752).—Chelidonic acid gives, with an aqueous solution of sodium chloride, a very sparingly soluble, characteristic, hyperacid salt, $\text{C}_7\text{H}_4\text{O}_6, \text{C}_7\text{H}_3\text{O}_6\text{Na}$. Pyrone is best prepared by distilling dry chelidonic acid with copper powder, which serves to equalise the temperature; like dimethylpyrone, it readily forms additive compounds with acids and with metallic salts.

The *hydrochloride*, $\text{C}_5\text{H}_4\text{O}_2, \text{HCl}$, precipitated on adding pyrone to hydrogen chloride in ether, melts at 139° , crystallises from alcohol, and is hygroscopic. Two oxalates of pyrone exist: the one, $\text{C}_5\text{H}_4\text{O}_2, \text{C}_2\text{H}_2\text{O}_4$, is obtained in ethereal solution, crystallises from water in leaflets, and melts at $136\cdot5^\circ$; the *other*, $3\text{C}_5\text{H}_4\text{O}_2, \text{C}_2\text{H}_2\text{O}_4$, is formed in aqueous solution, crystallises in thick, transparent prisms, and melts at 139° . Two crystalline *aurichlorides*, $3\text{C}_5\text{H}_4\text{O}_2, \text{HAuCl}_4$ and $2\text{C}_5\text{H}_4\text{O}_2, \text{HAuCl}_4$, may also be obtained; both melt at $116\cdot5^\circ$. The *picrate*, $\text{C}_{11}\text{H}_7\text{O}_9\text{N}_3$, crystallises from water or alcohol and melts at 129° . With calcium chloride in alcoholic solution, pyrone combines to form the crystalline additive compound, $2\text{C}_5\text{H}_4\text{O}_2, \text{CaCl}_2$, which deliquesces in the air. *Pyrene mercurichloride*, $\text{C}_5\text{H}_4\text{O}_2, \text{HgCl}_2$, crystallises in thin plates and melts at about 170° . *Pyrene silver nitrate*, $4\text{C}_5\text{H}_4\text{O}_2, 7\text{AgNO}_3$, melts and decomposes at 162° .

Pyrene does not combine with alkali hydroxides, but is decomposed by them. With potassium methoxide, however, in methyl alcohol, a colourless, crystalline compound, $\text{C}_5\text{H}_4\text{O}_2, \text{CH}_3\cdot\text{OK}$, is obtained; the sodium methoxide derivative, $\text{C}_5\text{H}_4\text{O}_2, \text{C}_2\text{H}_5\cdot\text{ONa}$, is formed similarly. With benzoyl chloride, pyrene potassium methoxide in ethereal suspension interacts to form a *methylbenzoate*, $\text{C}_{13}\text{H}_{12}\text{O}_4$, which crystallises from ether or alcohol in plates and melts at $98\cdot5$ — 99° . It is probable that the alkyloxide derivatives have the formula

$\text{O} \begin{array}{c} \text{CH:CH} \\ \text{CH:CH} \end{array} \text{C(OMe)}\cdot\text{OK}$, and the methylbenzoate the structure

$\text{O} \begin{array}{c} \text{CH:CH} \\ \text{CH:CH} \end{array} \text{C(OMe)}\cdot\text{OBz}$. It is thus the carbonyl group which reacts additively in these cases, whilst in the simple salts formed with acids the oxygen of the same group is perhaps quadrivalent; the hydrochloride, for instance, has probably the structure



Ethyl chelidonate combines additively with sodium ethoxide, but the product, unlike those obtained from pyrene, is soluble in ether, and therefore probably is formed by addition to the carbethoxyl radicle. With a large excess of mercuric chloride, the ester gives the compound $2\text{C}_{11}\text{H}_{12}\text{O}_6, \text{HgCl}_2$; with less mercuric chloride, the compound $4\text{C}_{11}\text{H}_{12}\text{O}_6, 3\text{HgCl}_2$, is obtained; both substances are crystalline. *Methyl chelidonate*, $\text{C}_9\text{H}_8\text{O}_6$, melts at $122\cdot5^\circ$. *Chelidonamide*, $\text{C}_5\text{H}_2\text{O}_2(\text{CO}\cdot\text{NH}_2)_2$, formed instantaneously by the action of ammonia on ethyl chelidonate dissolved in alcohol, crystallises from water in microscopic, infusible needles.

W. A. D.

Isomeric Coninium Iodides. MAX SCHOLTZ (*Ber.*, 1904, 37, 3627—3638).—By the interaction of *N*-ethylconiine and benzyl iodide, a mixture of two isomeric *benzylethylconinium iodides* is formed, which can be separated by means of chloroform. The α -iodide is sparingly soluble in chloroform and crystallises from water in colourless needles, melting at 178° and having $[\alpha]_D + 21.2^\circ$ at 20° in methyl alcohol; the β -iodide obtained on evaporating the chloroform mother liquors melts at 208° and has $[\alpha]_D + 31.2^\circ$ at 20°. The *platinichloride* of the α -chloride crystallises in prisms melting at 195°; the *platinichloride* of the β -chloride, which is sparingly soluble in water, from which it crystallises in rhombic prisms, blackens at 215° and melts at 218°. *N*-Benzylconiine, prepared by the action of benzylchloride and an alkali hydroxide on coniine, boils at 294—296° (corr.), has a sp. gr. 0.9461 at 20°/4°, and $[\alpha]_D 72.9^\circ$ at 20°; it reacts only very slowly with ethyl iodide. At temperature of the water-bath, the isomeric iodides are formed; at 120°, an interchange in position of the ethyl and benzyl groups takes place, resulting in the formation of ethylconiine hydroiodide.

In a similar manner, *isoamylconiine* and benzyl iodide react, forming isomeric *benzylisoamylconinium iodides*: the α -iodide crystallises from water in prisms melting at 169° and has $[\alpha]_D 26.6^\circ$ at 20°; the β -iodide crystallises from acetone in needles, melts at 185°, and has $[\alpha]_D + 33.3^\circ$ at 20°. The α -chloride forms a *platinichloride* sparingly soluble in hot water, from which it crystallises in rhombohedra melting at 188°; the β -iodide gives this salt, as well as a second, more soluble *platinichloride*, melting at 199°. The α -iodide forms a *picrate*, crystallising in prisms with pyramidal ends, melting at 129°, and this compound is also obtained from the β -iodide. *Benzylmethylconinium iodide* exists as an α -iodide melting at 187° and a β -form melting at 215°, only a relatively small proportion of the β -compound being formed.

Methyl benzylconiniumacetate iodide, $\text{CH}_3\text{Ph}\cdot\text{C}_9\text{H}_{16}\text{NI}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$, prepared from methyl coniine-*N*-acetate and benzyl iodide, also exists in two forms; the α -iodide melts at 103°, whilst the β -form crystallised from acetone melts at 146°. *Methylconiine-N-acetate* is a colourless liquid boiling at 244—245°, and having a sp. gr. 0.9726 at 20°/4° and $[\alpha]_D + 62.1^\circ$ at 20°. *Dibenzylconinium iodide* crystallises in prisms melting at 176°, and exists in one form only. E. F. A.

Certain Salts of Quinine. HENRI CARETTE (*J. Pharm. Chim.*, 1904, [vi], 20, 347—355).—When crystallised from water, normal quinine hydrochloride contains $2\frac{1}{2}\text{H}_2\text{O}$. This salt is hygroscopic, begins to melt at 80°, becomes brown at 215°, and above that temperature forms a black liquid. The water of crystallisation is lost at 102°, no hydrogen chloride being evolved, giving a yellow, anhydrous salt, which becomes colourless on cooling. When crystallised from alcohol, either absolute or 30 per cent., the salt contains 1.5 mols. alcohol, which is lost either at 100°, when some hydrogen chloride is given off, or in a vacuum. Too long heating or exposure to light renders the dry salt yellow. At 35—50° the salt loses its alcohol and yields by absorption of moisture the hydrochloride with $\frac{1}{2}\text{H}_2\text{O}$, which is more stable and

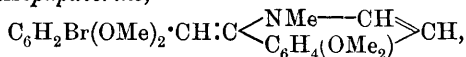
less hygroscopic than the anhydrous compound. The latter salt becomes yellow at 165—170°, forming a brown liquid at 180—185°, and has $[\alpha]_D - 233^\circ$.

Crystallographic measurements of the salt containing alcohol of crystallisation are given in the paper. G. D. L.

Papaverinium Bases. HERMAN DECKER (*Ber.*, 1904, 37, 3809—3815. Compare this vol., i, 338).—[With OSKAR KLAUSER.]—*Papaverine butyl bromide*, obtained by heating the components for 12 hours at 100°, is solid, melts at 109°, and then resolidifies and melts and decomposes on further heating at 217°. With alkalis, it yields the yellow *butylisopapaverine*, which is not readily obtained in a crystalline form. With dilute hydrochloric acid, it yields *papaverinium butyl chloride*, $C_{24}H_{30}O_4NCl \cdot 2H_2O$, melting at 131—132°. The *picrate* melts at 151—152°, the *mercurichloride* melts and decomposes at 200°, and the *platinichloride* at 204°.

Papaverine isobutyl iodide crystallises from alcohol in yellow, glistening prisms melting at 171—172°. *Papaverine p-nitrobenzyl chloride* melts and decomposes at 131°, the *mercurichloride* melts at 188°, the *picrate* at 183—184°. On treatment with alkali, the chloride does not yield a yellow *iso-base*, but is completely decomposed, turning black and evolving ammonia. *Papaverine isopropyl iodide* melts at 93—94°.

[With M. GIRARD.]—Bromopapaverine has been prepared by a modification of Anderson and Goldschmidt's method (*Monatsh.*, 1885, 6, 674). Its *hydrochloride* melts sharply at 197°, the *picrate* melts and decomposes at 125°. The bromine is not removed by treatment with alkali at 200°. The brominated base yields a *methiodide* crystallising in yellow cubes and melting and decomposing at 225°. The base also combines directly with methyl sulphate without any solvent, and the aqueous solution of the product on treatment with alkali yields *N-methyl bromisopapaverine*,



which forms yellow crystals melting at 122° and is much more stable than the *iso-bases* previously obtained. It combines but slowly with water, and is only slowly oxidised by atmospheric oxygen.

Bromopapaverine benzyl chloride, on treatment with alkali, yields *N-benzylbromoisopapaverine*, which crystallises in yellow needles melting at 113°. It is stable, and on oxidation with permanganate yields 6-bromoveratric acid (Koelle, *Ber.*, 1878, 136) and 6:7-dimethoxy-2-benzyl-1-isoquinolone (this vol., i, 339).

When less permanganate is used, 6-bromoveratraldehyde melting at 150° is obtained. The bromo-acid melts at 186°. J. J. S.

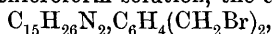
Products of the Addition of Alkyl Haloids to Sparteine. MAX SCHOLTZ and P. PAWLICKI (*Arch. Pharm.*, 1904, 242, 513—520).—An attempt was made to find whether the two nitrogen atoms in the diacid tertiary base sparteine have a similar function, by adding 1 mol. each of two different alkyl iodides in succession, the order of succession being varied, and noting whether the final products in the two cases were isomeric or identical; they were found to be isomeric. Sparteine monomethiodide (Bamberger, *Abstr.*, 1887, 163), melting at

234°, unites with ethyl iodide to form a *compound* melting at 239°, whereas the *compound* formed from the monoethiodide (which melts at 231°) and methyl iodide melts at 246°, and a mixture of the two compounds has an ill-defined melting point at about 15° lower. *Sparteine monobenzyl iodide* melts at 230°, the *compound* of this with methyl iodoacetate at 219°; the additive *product* from the alkaloid and 1 mol. of methyl iodoacetate melts at 230°, the *compound* of this with benzyl iodide at 245°. The *compound* of the monomethiodide with methyl iodoacetate melts at 232°, the *compound* from the methyl iodoacetate additive product and methyl iodide at 249°.

The compound $C_{15}H_{26}N_2, MeI, HI$, however, obtained by the action of methyl iodide on sparteine hydriodide, is identical, not isomeric, with that obtained from sparteine and methyl iodide in methyl alcoholic solution at 100°, in which circumstances the monomethiodide is first formed, for it is the final product in the cold.

When the compound $C_{15}H_{26}N_2, MeI, HI$ is decomposed with concentrated aqueous potassium hydroxide, sparteine monomethiodide is precipitated, identical with that obtained from sparteine and methyl iodide in the absence of alcohol; no sparteine is precipitated, contrary to Bamberger's statement.

With *isoamyl iodide*, sparteine yields *compounds* containing 1 or 2 mols. of the iodide according to the proportions employed; these melt at 229° and 230° respectively. In the presence of alcohol, the compound $C_{15}H_{26}N_2, C_5H_{11}I, HI$, melting at 227°, is formed. With *o*-xylylene bromide in chloroform solution, the compound



melting at 237°, is formed.

C. F. B.

Action of Pyrocinchonic Anhydride on the Phenylene-diamines. LUCIANO ROSSI (*Real. Accad. Sci. Fis. Mat. Napoli*, 1904, [iii], 10, 122—132).—The author has prepared *o*-phenylenepyrocinchonic diamide and *m*- and *p*-aminophenylenepyrocinchonimides by the action, either alone or in alcoholic solution, of molecular proportions of pyrocinchonic anhydride and the particular phenylenediamine. These compounds are all soluble in alcohol, acetone, benzene, or chloroform.

o-Phenylenepyrocinchonic diamide, $C_6H_4 \begin{smallmatrix} \text{NH} \cdot \text{CO} \cdot \text{CMe} \\ \text{NH} \cdot \text{CO} \cdot \text{CMe} \end{smallmatrix}$, crystallises from alcohol in yellow prisms melting at 150—154°.

m-Aminophenylenepyrocinchonimide, $NH_2 \cdot C_6H_4 \cdot N \begin{smallmatrix} \text{CO} \cdot \text{CMe} \\ \text{CO} \cdot \text{CMe} \end{smallmatrix}$, forms greenish-yellow crystals melting at 160°.

p-Aminophenylenepyrocinchonimide, $NH_2 \cdot C_6H_4 \cdot N \begin{smallmatrix} \text{CO} \cdot \text{CMe} \\ \text{CO} \cdot \text{CMe} \end{smallmatrix}$, crystallises in golden-yellow needles melting at 140°.

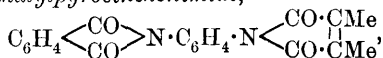
By using two mols. of pyrocinchonic anhydride to one of the phenylenediamine, the following di-acid imides were obtained:

Phenylene-o-dipyrocinchonimide, $C_6H_4 \left(N \begin{smallmatrix} \text{CO} \cdot \text{CMe} \\ \text{CO} \cdot \text{CMe} \end{smallmatrix} \right)_2$, crystallises in tufts of white needles melting at 139—140°.

Phenylene-m-dipyrrocinchonimide, $C_{18}H_{16}O_4N_2$, crystallises from alcohol in tufts of faintly cream-coloured needles melting at 175° .

Phenylene-p-dipyrrocinchonimide, $C_{18}H_{16}O_4N_2$, crystallises in pale cream needles or, from acetone, in hexagonal prisms, which begin to turn brown at 200° and melt at 285° .

m-Phenylenephthalylpyrocinchonimide,

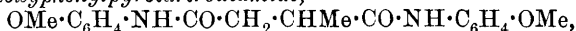


crystallises from alcohol or acetone in white needles and from benzene in small prisms, which melt at 212° and are soluble in chloroform.

p-Phenylenephthalylpyrocinchonimide, $C_{20}H_{14}O_4N_2$, crystallises from benzene in white needles, which begin to turn brown at above 200° and melt at $274-275^\circ$; it is soluble in chloroform and to a slight extent in alcohol or acetone. T. H. P.

Action of Pyruvic and Pyrotartaric Acids on the *p*-Aminophenols. G. GIUFFRIDA and A. CHIMIENTI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1904, [iii], 10, 109—121).—*p-Hydroxyphenylpyrotartrimide*, $\begin{array}{c} CHMe \cdot CO \\ | \\ CH_2 - CO \end{array} > N \cdot C_6H_4 \cdot OH$, prepared by the action of either pyruvic or pyrotartaric acid on *p*-aminophenol, separates from water or alcohol in crystals melting at 230° .

p-Methoxyphenylpyrotartrodiamide,

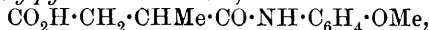


obtained by the action of either pyruvic or pyrotartaric acid on *p*-anisidine, crystallises from alcohol in pearly white needles melting at $241-242^\circ$. When heated in a sealed tube with concentrated hydrochloric acid at 110° , it yields pyrotartaric acid, *p*-aminophenol hydrochloride, and methyl chloride. The *dinitro*-derivative, $C_{19}H_{20}O_4N_2(NO_2)_2$, is deposited from acetic acid solution in minute, yellow crystals melting at 202° , and the *dibromo*-compound, $C_{19}H_{20}O_4N_2Br_2$, crystallises in small, yellow needles melting at $82-83^\circ$.

p-Methoxyphenylpyrotartrimide, $\begin{array}{c} CHMe \cdot CO \\ | \\ CH_2 - CO \end{array} > N \cdot C_6H_4 \cdot OMe$, the prin-

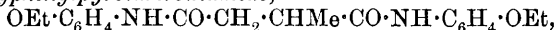
cipal product of the interaction of pyrotartaric acid and *p*-anisidine, crystallises from alcohol in white prisms melting at 95° ; it has the normal molecular weight in freezing benzene.

p-Methoxyphenylpyrotartramic acid,



obtained by the action of alcoholic potassium hydroxide on *p*-methoxyphenylpyrotartrimide, forms crystals melting at 137° .

p-Ethoxyphenylpyrotartrodiamide,



prepared by the interaction of pyruvic or pyrotartaric acid and *p*-phenetidine, crystallises from alcohol in long, white needles melting at $234-235^\circ$ and soluble in acetic acid. When heated in a sealed tube with concentrated hydrochloric acid, it yields pyrotartaric acid, *p*-aminophenol hydrochloride, and ethyl chloride. The *nitro*-derivative, $C_{21}H_{25}O_4N_2 \cdot NO_2$, separates from acetic acid in minute crystals, melt-

ing at 195° ; the bromo-compound, $C_{21}H_{25}O_4N_2Br$, crystallises from alcohol in milk-white, silky needles, melts at 74° , and is extremely soluble in alcohol.

p-Ethoxyphenylpyrotartride, $C_3H_6\left<\begin{smallmatrix} CO \\ CO \end{smallmatrix}\right>N\cdot C_6H_4\cdot OEt$, obtained by the action of pyrotartaric acid on *p*-phenetidine, is deposited from alcohol in crystals melting at 97° .

p-Methoxyphenyliminopyruvic acid, $CO_2H\cdot CMe\cdot N\cdot C_6H_4\cdot OMe$, prepared by the action of pyruvic acid on *p*-anisidine in alcoholic solution, is obtained as an amorphous, yellow product which is insoluble in the ordinary solvents and decomposes, giving pyrotartrodiamide, on heating.

p-Ethoxyphenyliminopyruvic acid, $CO_2H\cdot CMe\cdot N\cdot C_6H_4\cdot OEt$, prepared from pyruvic acid and *p*-phenetidine, is a yellow, amorphous substance, which begins to melt at 105° and is completely fused at about 228° .

T. H. P.

Preparation of Pure *iso*Stilbazoline. ALBERT LADENBERG (*Ber.*, 1904, 37, 3688—3692. Compare Abstr., 1903, i, 275, and this vol., i, 92).—*d*- and *l*-Stilbazolines have been obtained by the aid of the acid tartrates, namely, *d*-stilbazoline hydrogen *l*-tartrate and *l*-stilbazoline hydrogen *d*-tartrate. The values of $[\alpha]_D$ for the free bases at 18° are respectively $+12.16^{\circ}$ and -11.5° . The sp. gr. is 0.9699.

When the two bases are mixed, no rise in temperature occurs and hence no true racemic compound is formed.

To obtain *isostilbazoline*, the acid *d*-tartrates are first prepared, the *l*- and *iso*-bases are precipitated as salts, and the *d*-base remains in solution. The mixed *d*- and *iso*-bases are then converted into normal *l*-tartrates, when the *isostilbazoline l*-tartrate crystallises out, even when the solution is fairly strongly acid (1—3 mols. of base to 1 mol. of acid). This salt forms colourless, hexagonal plates and melts at 214 — 215° . The base has $[\alpha]_D - 5.82^{\circ}$, a sp. gr. 0.9727 at 19° , and it distils at 162° under 26 mm. pressure. The base may also be isolated in the form of its *d*-camphorsulphonate.

The normal *l*-tartrate of *l*-stilbazoline crystallises also in six-sided plates, melts at 211 — 212° , and contains $\frac{1}{2}H_2O$. It is not readily precipitated in acid solution, and thus differs from the corresponding salt of the *iso*-base.

One hundred parts of water at 17° dissolve 12.96 parts of the salt of *l*-base or 12.05 parts of the salt of the *iso*-base.

The *hydrochlorides* of the two bases are similar; they crystallise from acetone in colourless needles or prisms; that of the *l*-base melts at 149 — 150° and that of the *iso*-base at 150 — 151° . The *aurichlorides* are also similar, and melt at 116 — 117° and 117 — 118° respectively.

J. J. S.

[Coloured Quinoline Derivatives.] FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 154448).—Alcoholic potassium hydroxide converts the alkyl iodides and chlorides of quinoline, and such of its derivatives as contain no methyl group in the pyridine ring, into dyes, which are not identical with the cyanines. In each case, a red and a

yellow dye are obtained, both of which may be used in the preparation of orthochromatic photographic plates. The appearance and solubility of a number of these derivatives is described. C. H. D.

Mechanism and Limits of the Phthalone Reaction. ALEXANDER EIBNER (*Ber.*, 1904, 37, 3605—3612).—The methyl group in quinaldine reacts with phthalic anhydride to form the compound $C_9NH_6 \cdot CH_2 \cdot C(OH) \langle \overset{C_6H_4}{\underset{O}{\text{---}}} \rangle CO$, where one of the two carbonyl groups in phthalic anhydride reacts, and also quinolylacetophenone-carboxylic acid, $CO_2H \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot C_9NH_6$ (compare Eibner and Lange, *Abstr.*, 1901, i, 348). In the production of quinophthalone, the former product is first formed, from which an asymmetric quinophthalone (quinophthalide) results; then follows the formation of quinolylacetophenonecarboxylic acid, which afterwards yields a symmetric quinophthalone. The first three of these stages occur between 100° and 155° ; the final stage is complete at about 210° .

Quinaldine condenses with benzaldehyde much more readily than does lepidine. A similar variance in the behaviour of quinaldine and lepidine is shown by the behaviour with phthalic anhydride. Whilst the former yields quinophthalone, the latter, when heated with a molecular amount of phthalic anhydride at 240° for 3 hours, forms a tarry mass, which gives no phthalone reaction. The question is discussed as to which ring compounds besides quinaldine are capable of yielding phthalones.

Naphthalic anhydride condenses with quinaldine to form *quinonaphthalone*, which forms yellow needles and melts at 256° .

A. McK.

Derivatives of 2-Amino-5-ethoxyphenol. FERDINAND HENRICH and F. SCHIERENBERG (*J. pr. Chem.*, 1904, [ii], 70, 325—331. See this vol., i, 1006).—2-Amino-5-ethoxyphenol, obtained by reduction of α -nitrosoresorcinol ethyl ether (Kietaihl, *Abstr.*, 1899, i, 344), yields 4-aminoresorcinol when heated with concentrated hydrochloric acid in a sealed tube at 150° . The action of benzoyl chloride on 2-amino-5-ethoxyphenol in 10 per cent. sodium hydroxide solution leads to the formation of a *monobenzoyl* derivative which melts at 187° and, when distilled, yields 5-ethoxy-1-phenylbenzoxazole, $OEt \cdot C_6H_3 \langle \overset{N}{\underset{O}{\text{---}}} \rangle C \cdot C_6H_5$, which is also formed when the hydrochloride of 2-amino-5-ethoxyphenol is heated with benzoyl chloride. It forms glistening, broad crystals, melts at 64 — 66° , and dissolves easily in organic solvents and in concentrated sulphuric acid to fluorescent solutions. The *diacetyl* derivative of 2-amino-5-ethoxyphenol, formed when the hydrochloride is heated with acetic anhydride, crystallises in thick prisms and melts at 91 — 93° . Along with the diacetyl compound, there is formed a small quantity of a *substance* which melts at 132° .

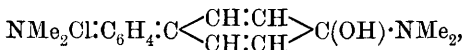
When oxidised by a current of air passed through its solution in aqueous sodium hydroxide, 2-amino-5-ethoxyphenol yields the

phenoxazine derivative, $\text{OEt} \cdot \text{C}_6\text{H}_3 \langle \text{N} \rangle \text{C}_6\text{H}_2\text{O} \cdot \text{NH}_2$, which forms red crystals, melts at 280° , dissolves in sulphuric acid to a violet solution which becomes red on dilution, and yields an *acetyl* derivative, $\text{C}_{16}\text{H}_{14}\text{O}_4\text{N}_2$, which crystallises from a mixture of glacial acetic acid and acetic anhydride. The *hydrochloride*, $\text{C}_{14}\text{H}_{12}\text{O}_3\text{N}_2 \cdot \text{HCl}$, is dark violet and is hydrolysed by boiling, more slowly by cold water.

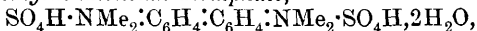
G. Y.

Quinonoidal Derivatives of Benzidine. I. RICHARD WILLSTÄTTER and LUDWIG KALB (*Ber.*, 1904, **37**, 3761—3775).—Dimethylaniline is instantaneously oxidised by potassium permanganate in presence of dilute sulphuric acid, giving diphenoquinonetetramethyldi-imonium disulphate (*infra*), which, by reduction with sulphurous acid, is easily converted into tetramethylbenzidine, $\text{C}_{12}\text{H}_8(\text{NMe}_2)_2$; the latter substance is easily prepared in this way and melts at 193.5° (Michler gives 195° , Ullmann, this vol., i, 269, gives 197°).

The green substance formed by the oxidation of tetramethylbenzidine with ferric chloride (Lauth, *Abstr.*, 1891, 457) has the probable composition $\text{C}_{16}\text{H}_{21}\text{ON}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, rather than that assigned to it by Lauth; its purification is difficult, as it is comparatively unstable. It probably has the constitution

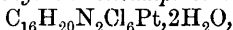


of a quinoneimonium salt containing an imino- ψ -quinol radicle. The green salt is converted by an excess of hydrochloric acid into an orange-coloured salt, which, however, is stable only in presence of this excess and cannot be isolated. But the corresponding sulphate, *diphenoquinonetetramethyldi-imonium disulphate*,

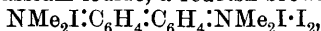


is obtained by passing an excess of chlorine through a solution of tetramethylbenzidine in alcoholic sulphuric acid; it crystallises in red prisms, decomposes gradually in moist air, and dissolves in water giving an intensely orange-coloured solution.

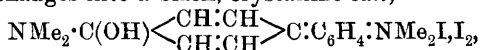
Diphenoquinonetetramethyldi-imoniumplatinichloride,



is obtained by dissolving the foregoing green salt in hydrochloric acid, which turns it into the orange dichloride, and adding platinic chloride; it forms slender, dark violet-coloured needles and is more stable than the other salts. On mixing the green chloride dissolved in hydrochloric acid with potassium iodide, a reddish-brown *periodide*,



is obtained; with an excess of water containing hydrochloric acid, this salt suddenly changes into a black, crystalline salt,

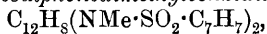


belonging to the same series as the green chloride already described.

The green diphenoquinonetetramethyldi-imonium chloride is converted by an excess of gaseous sulphur dioxide, or by a solution of sodium sulphate to which acid is added, into *tetramethylbenzidine sulphonic acid*, $\text{C}_{16}\text{H}_{20}\text{O}_3\text{N}_2\text{S}$; this crystallises from dilute acetic acid in

colourless, six-sided leaflets, from alcohol in small rhombohedra or in needles, melts and decomposes at 261.5° , and gives crystalline *sodium*, *potassium*, and *ammonium* salts. The same acid may be obtained by directly sulphonating tetramethylbenzidine.

s-Dimethylbenzidine is prepared by the following method. Benzidine is converted by means of toluene-*p*-sulphonic chloride into ditoluene-*p*-sulphonebenzidine, $C_{12}H_8(NH \cdot SO_2 \cdot C_7H_7)_2$, which crystallises from acetone, on diluting, in large leaflets and melts at 243° ; this substance is methylated in alkaline acetone solution by means of methyl sulphate, the product, *di-p-toluenesulphonatedimethylbenzidine*,



crystallising from glacial acetic acid in aggregates of leaflets and melting at 235° . *Dimethylbenzidine*, $C_{12}H_8(NHMe)_2$, obtained by its decomposition with dilute sulphuric acid, crystallises from dilute alcohol, melts at $74-76^{\circ}$, and gives a crystalline *hydrochloride* melting at 149° . The green oxidation product of dimethylbenzidine obtained by the addition of ferric chloride has the composition $C_{14}H_{17}ON_2Cl$, and is converted by hydrochloric acid and platinic chloride into *diphenoguinone-dimethyldi-imonium platinichloride*, $C_{14}H_{16}N_2Cl_6Pt, H_2O$, which forms golden-brown prisms.

W. A. D.

A New Application of the Pyridine Method of Acylation. KARL AUWERS (*Ber.*, 1904, 37, 3899—3903. Compare this vol., i, 736, and Dieckmann, this vol., i, 845, 873).—In the treatment of hydroxyl compounds containing a basic group with acyl chlorides, the acylation commences as a general rule in the basic group, the hydroxyl only being attacked subsequently. The direct preparation of *O*-acyl derivatives has therefore only been possible in such cases when the basic group has been protected by neighbouring groups, as in *o*-hydroxybenzyl-*o*-nitroaniline. It is now found that the preparation of *O*-acyl derivatives may be effected by the pyridine method, provided that the compound has acid properties and that the basic properties of the second constituent are not too pronounced. When these conditions are not fulfilled, either the *N*-derivatives or the mixed *ON*-diacyl derivatives are obtained.

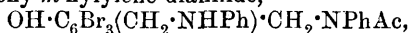
A large excess of acyl chloride is usually required, and the *O*-derivatives obtained remain unchanged when treated with an excess of acyl chloride in pyridine solution, whereas *N*-derivatives are readily converted under the same conditions into diacyl derivatives. The reaction is in some cases complicated by the occurrence of secondary reactions due to the presence of the pyridine (compare succeeding abstracts).

C. H. D.

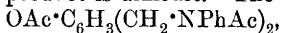
Transformation of *O*-Acyl Compounds into *N*-Derivatives. KARL AUWERS (*Ber.*, 1904, 37, 3903—3905).—It has been shown (this vol., i, 736) that phenol esters undergo a transformation into *N*-derivatives when a group NHR occupies the ortho-position with respect to the phenolic hydroxyl, or the α -position in an ortho-side-chain, R being hydrogen, or an alkyl or aryl group. The transformation usually occurs so rapidly that it is not possible to isolate the *O*-derivative. It is

now found (compare succeeding abstracts) that the *O*-acetates of *O*-hydroxyaldehyde phenylhydrazones are stable, but are converted into *N*-derivatives by boiling with either glacial acetic acid or pyridine. The reaction cannot be explained by the occurrence of hydrolysis, but must be regarded as an intramolecular rearrangement which is accelerated by those reagents. C. H. D.

Observations on Acylation. KARL AUWERS and R. BONDY [and, in part, K. MÜLLER] (*Ber.*, 1904, **37**, 3905—3915).—The *N*-acetate of tribromo-*p*-hydroxy-*m*-xylylene dianilide,



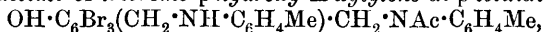
was found by Auwers and Hampe (*Abstr.*, 1900, i, 96) to yield only a diacetate on further acetylation, although there should be in this case no steric hindrance. It is now found that a triacetate may be prepared by heating with acetic anhydride and sodium acetate, although the purification of the product is difficult. The *triacetate*,



crystallises slowly from light petroleum containing a little benzene in flat, glistening needles and melts at 145°. It separates from alcohol or ether in snow-white needles containing solvent of crystallisation.

Dilute sulphuric acid removes 1 mol. of acetic acid, as may be determined by titration, but only a charred product remains. Fusion at 200° with potassium hydroxide hydrolyses the triacetate to the *NN*-diacetate, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{CH}_2\cdot\text{NPhAc})_2$, crystallising from alcohol in long, flat tablets, melting at 207—208°, and dissolving moderately in benzene, alcohol, or acetic acid, sparingly in ether or light petroleum. The isomeric *ON*-diacetate, obtained by adding acetyl chloride to the monoacetate dissolved in pyridine, and extracting the product with alcohol to remove triacetate, crystallises from alcohol in small, well-formed leaflets, melts at 200—201°, and dissolves readily in benzene or chloroform, moderately in acetic acid or ethyl acetate, sparingly in alcohol.

The *N*-acetate of tribromo-*p*-hydroxy-*m*-xylylene di-*p*-toluidide,



prepared from *p*-toluidine and pentabromo-*m*-xylenol acetate, crystallises from toluene in groups of slender, white needles melting at 206°, and dissolves readily in acetone, acetic acid, ethyl acetate, or chloroform, less readily in alcohol or benzene. The *triacetate* crystallises from light petroleum-benzene in pearly prisms melting at 154° and yielding an *NN*-diacetate on hydrolysis, which, however, was only obtained in an amorphous form. The *ON*-diacetate, obtained by acetylating the monoacetate in pyridine solution, forms pearly leaflets and melts at 187—188°.

The *N*-acetate of the corresponding *o*-toluidide crystallises from benzene in thick, glistening prisms melting at 190—191°; the *ON*-diacetate separates from alcohol in leaflets and melts at 193°.

The compounds described by Biltz and Grimm (*Abstr.*, 1899, i, 502) as monoacetates of the phenylhydrazones of the two *m*-nitrosalicylaldehydes are found to be *ON*-diacetates.

It was not found possible to acetylate 5-nitro-3-methylsalicylaldehyde, although the two isomeric compounds, in which the hydroxyl is

also situated between two ortho-groups, readily yield triacetates (compare following abstract). C. H. D.

Phenylhydrazones of Aromatic Hydroxyaldehydes. I. KARL AUWERS and R. BONDY (*Ber.*, 1904, 37, 3915—3929. Compare preceding abstracts).—The hydroxyaldehydephenylhydrazones investigated yield *N*-acetates with acetic anhydride and *ON*-diacetates on further acetylation. With acetyl chloride in pyridine solution, on the other hand, they yield almost exclusively *O*-acetates. The *O*-acetates of ortho-compounds may undergo a rearrangement to *N*-acetates, while the para-derivatives are stable.

5-Nitro-2-hydroxy-3-methylbenzaldehyde, prepared by nitrating *o*-homosalicylaldehyde, crystallises from light petroleum in slender, white needles, melting at 134° and becoming yellow after a time, or from glacial acetic acid in pale yellow scales. The *phenylhydrazone*, $C_{14}H_{13}O_3N_3$, crystallises from acetic acid, alcohol, or benzene in yellow, highly refractive needles melting at 206—207°. Moist ether converts it into red crystals of a *compound*, $C_{14}H_{15}O_4N_3$, which is probably a hydrate. Heat, or crystallisation from solvents, converts the red modification into the yellow. The *N*-acetate forms long, white, silky needles and melts at 241—242°. Sodium hydroxide does not dissolve the crystalline compound, but when precipitated by water from alcoholic solution it dissolves readily and may be reprecipitated by carbon dioxide. The *N*-acetate may also be prepared synthetically from the nitroaldehyde and α -acetylphenylhydrazine, $NPhAc \cdot NH_2$.

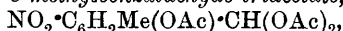
The *O*-acetate, obtained by acetylation in pyridine solution, exists in two modifications, one of which forms red plates or broad needles and melts at 205—206°, while the second forms yellow crystals, passing into the red modification at 175° and dissolving more readily in alcohol or benzene than the red crystals. The nature of the isomerism has not been determined.

Warming with pyridine or glacial acetic acid partially converts the *O*-acetate into the *N*-acetate.

The *ON*-diacetate crystallises from alcohol in slender, white needles and melts at 199—200°.

The *phenylhydrazone* of *3-nitro-2-hydroxy-5-methylbenzaldehyde*, $C_{14}H_{13}O_3N_3$, crystallises from alcohol in yellow plates and melts at 164—166°. The *N*-acetate forms thick, yellow crystals melting at 252—253°, previously softening, and dissolves readily in sodium hydroxide, sparingly in organic solvents. It may also be prepared synthetically by means of α -acetylphenylhydrazine. The *O*-acetate crystallises from acidified alcohol in silky, yellow, felted needles melting at 155—156°. The *ON*-diacetate forms yellow needles, melting slowly at 130—150° and possibly consisting of a mixture of isomerides.

3-Nitro-2-hydroxy-5-methylbenzaldehyde triacetate,



crystallises from a mixture of benzene and light petroleum in rosettes of thick, white needles melting at 132—132.5°.

3-Nitro-4-hydroxy-5-methylbenzaldehydephenylhydrazone crystallises from acetic acid in orange, hexagonal plates melting at 153—155°.

The *N*-acetate forms glistening, golden needles and melts at 188—189°. The *O*-acetate forms flat, orange needles and leaflets melting at 162—163°. It was not found possible to convert the *O*-acetate into the *N*-derivative.

3-Nitro-4-hydroxy-5-methylbenzaldehyde triacetate forms colourless plates melting at 117—118°. C. H. D.

Phenylhydrazones of Aromatic Hydroxyaldehydes. II. KARL AUWERS and O. BÜRGER (*Ber.*, 1904, 37, 3929—3937. Compare preceding abstract).—5-Nitrosalicylaldehydephenylhydrazone *O*-acetate, prepared by acetylation in pyridine solution, separates from alcohol in ruby-red needles or from chloroform in orange, silky leaflets. A small quantity of the *N*-acetate is produced at the same time, and may also be prepared by heating the *O*-acetate with acetic acid. It crystallises from ethyl acetate in slender, white needles and melts at 165°. The *ON*-diacetate was prepared by Biltz and Grimm (*Abstr.*, 1899, i, 502), but erroneously described by them as a monoacetate.

5-Nitrosalicylaldehyde triacetate, $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{OAc})\text{CH}(\text{OAc})_2$, forms colourless, rhombic prisms melting at 114—115°.

6-Nitrosalicylaldehydephenylhydrazone *ON*-diacetate is identical with Biltz and Grimm's monoacetate.

3-Nitro-4-hydroxybenzaldehydephenylhydrazone *O*-acetate forms orange needles melting at 134—135°. The *N*-acetate forms golden needles melting at 193—194°; the *ON*-diacetate forms yellow needles.

5-Bromosalicylaldehydephenylhydrazone forms flat, yellow needles melting at 151°. The *O*-acetate forms glassy, yellow needles melting at 138°; the *N*-acetate forms long, white, felted needles melting at 152°; the *ON*-diacetate forms flat, white needles and melts at 136—137°.

5-Bromo-3-nitrosalicylaldehyde, obtained by the nitration of bromosalicylaldehyde, crystallises from benzene-light petroleum in yellow needles melting at 147—148°. The phenylhydrazone forms large, dark brown needles melting at 243°. It yields an *O*-acetate, crystallising in red needles and melting at 209—210°; an *N*-acetate, forming colourless needles melting at 248°; and an *ON*-diacetate forming pale yellow needles melting at 203—204°. C. H. D.

Acylation of Compounds with Mixed Functions. KARL AUWERS and K. SONNENSTUHL (*Ber.*, 1904, 37, 3937—3943).—Benzoylation of salicylaldehydephenylhydrazone in pyridine solution yields only the *O*-benzoate, crystallising from alcohol in colourless tablets melting at 148—149°. Boiling with aniline or pyridine does not cause rearrangement to an *N*-derivative, but partially regenerates the hydrazone, forming the *ON*-dibenzoate, which crystallises in colourless needles and melts at 170—171°.

p-Hydroxybenzaldehydephenylhydrazone also yields an *O*-benzoate, crystallising in bundles of glistening needles and melting at 166—167°.

Dibromo-*p*-hydroxy- ψ -cumylaniline, $\text{OH} \cdot \text{C}_6\text{H}_2\text{Br}_2\text{Me}_2 \cdot \text{CH}_2 \cdot \text{NHPh}$, yields an *O*-benzoate melting at 174—175°. The *N*-benzoate, prepared by Claisen's method, melts at 163—165°.

Dibromo-*o*-hydroxybenzylaniline, on the other hand, yields on benzylation in pyridine solution the *N*-benzoate, melting at 167—168°, in consequence of the intramolecular rearrangement undergone by ortho-derivatives (compare this vol., i, 736).

p-Aminophenol yields the *ON*-dibenzoate, together with some *N*-benzoate melting at 213°.

m-Aminobenzyl alcohol yields only the *ON*-dibenzoate melting at 113—114°. Alcoholic sodium hydroxide converts it into the *N*-benzoate melting at 115°.

Hydroxyethylamine yields the *ON*-dibenzoate. Diphenylhydroxyethylamine, $\text{OH}\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{NH}_2$, yields only the *N*-benzoate (Söderbaum, Abstr., 1896, i, 483). *iso*Diphenylhydroxyethylamine *N*-benzoate, prepared by partial hydrolysis of the dibenzoate, melts at 223°. C. H. D.

Mutual Replacement of Hydrazine Residues in Hydrazones and Osazones. EMIL VOTOČEK and R. VONDRÁČEK (*Ber.*, 1904, 37, 3848—3854. Compare Ofner, this vol., i, 936).—Two isomeric mixed osazones may be obtained by the action of phenylmethylhydrazine acetate on dextrosephenylhydrazine or on lævulosephenylhydrazine. The one (A) melting at 192° is regarded as $\alpha\beta$ -diphenyl- β -methylglucosazone, and the one melting at 205° (B) as $\alpha\beta$ -diphenyl- α -methylglucosazone. The formation of these isomerides indicates that the hydrazine groups are only loosely combined in the hydrazone, and this has been confirmed by the replacement of one hydrazine residue by another in various phenylhydrazones and osazones. As a rule, the replacement does not occur with alcoholic solutions, but readily in the presence of acetic acid. Benzaldehydephenylmethylhydrazine is readily transformed into the corresponding phenylhydrazine, and this, in its turn, can be converted back into the phenylmethylhydrazine. An aqueous solution of galactosephenylhydrazine with phenylmethylhydrazine acetate at the ordinary temperature yields the phenylmethylhydrazine. Arabinosephenylmethylhydrazine can be obtained in a similar manner. Dextrosephenylhydrazine can be transformed into the β -naphthylhydrazine in alcoholic solution at the ordinary temperature without the aid of acetic acid. Galactosephenylbenzylhydrazine under similar conditions yields the phenylmethylhydrazine.

Phenylmethylhydrazine does not appear to react with galactose-*p*-bromophenylhydrazine or diphenylhydrazine with dextrosephenylmethylhydrazine. Glyoxalphenylosazone and phenylmethylhydrazine acetate yield glyoxalphenylmethylosazone. Phenylglucosazone and phenylmethylhydrazine yield the mixed osazones melting at 205°.

J. J. S.

Separation and Isolation of Reducing Sugars by means of Aromatic Hydrazines. EMIL VOTOČEK and R. VONDRÁČEK (*Ber.*, 1904, 37, 3854—3858).—The sugars contained in mixtures may readily be separated and isolated in the form of hydrazones by the addition of first one aromatic hydrazine and then a second. When an acetic acid solution of phenylhydrazine is added to an aqueous solution

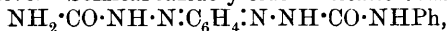
containing both *d*-mannose and *d*-galactose, pure *d*-mannosephenylhydrazone is precipitated, and, on the addition of phenylmethylhydrazine to the filtrate, galactosephenylmethylhydrazone crystallises out. *d*-Galactose and dextrose can be separated by first adding phenylmethylhydrazine and then phenylhydrazine to the filtrate. *d*-Arabinose and dextrose, rhodose and dextrose can be separated in exactly the same way, and *d*-mannose and *d*-arabinose or *d*-mannose and rhodose by first adding phenylhydrazine and then phenylmethylhydrazine to the filtrate. Galactose and rhamnose may be separated by the aid of phenylmethylhydrazine alone, as rhamnosephenylmethylhydrazone is very readily soluble in dilute alcohol.

Arabinosediphenylhydrazone and a small amount of galactosephenylmethylhydrazone have been obtained from the hydrolytic products of "arabic acid." Mannose and dextrose could not be detected. Arabinose, galactose, and dextrose can be detected in the hydrolytic products of gum arabic, but no mannose.

Hydrolysed coffee beans yield mannosephenylhydrazone, arabinosediphenylhydrazone, and galactosephenylmethylhydrazone. J. J. S.

Relation between Quinonehydrazones and *p*-Hydroxyazo-compounds. I. Constitution of the so-called Quinonemonosemicarbazones. WALTHER BORSCHÉ [with T. ZELLER] (*Annalen*, 1904, 334, 143—200).—Since it would seem probable that the *p*-hydroxyazo-compounds would exist in the isomeric quinonehydrazone form when the azo-group is linked not with two similar groups, as, for example, two phenyl groups, but with two dissimilar groups, one aromatic, and the other of some different character, a series of quinonemonophenylcarbamic hydrazones have been prepared and studied.

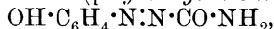
Benzoquinonephenylcarbamic hydrazone (*p*-hydroxybenzeneazofor-manilide), $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{CO}\cdot\text{NHPh}$ or $\text{O}:\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$, prepared from benzoquinone and the hydrochloride of phenylcarbamic hydrazide, crystallises in yellowish-red prisms, melting and decomposing at 185° , and is soluble in dilute alkali hydroxides and concentrated acids; the sodium salt is a dark red, crystalline mass. Phenylhydrazine acts as a reducing agent, converting the *p*-hydroxybenzeneazofor-manilide into the *p*-hydroxyphenylhydrazide of phenylcarbamic acid, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$, which is also produced by reduction with zinc dust and acetic acid; it crystallises in needles melting and decomposing at 207° , and is reconverted by the air into the azo-derivative. Semicarbazide yields a *disemicarbazone*,



in the form of a red, crystalline powder, melting and decomposing at 242° and soluble in alkali hydroxides. Phenylsemicarbazide produces the *quinonediphenylsemicarbazone*, $\text{C}_6\text{H}_4(\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh})_2$, which decomposes at 249 — 250° . Neither of the reactions just mentioned throws any decisive light on the constitution of the hydroxyazo-compound, since *p*-ethoxybenzeneazofor-manilide behaves in an exactly similar manner. On brominating *p*-hydroxybenzeneazofor-manilide in acetic acid solution in the presence of sodium acetate, 4-hydroxy-3:5-dibromobenzenazofor-manilide, $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{N}:\text{N}\cdot\text{CO}\cdot\text{NHPh}$,

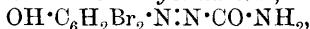
is obtained as yellow needles melting and decomposing at 226—227°; when decomposed by alkali hydroxides, it yields 2:6-dibromophenol (m. p. 56°). This reaction points to the original *p*-hydroxybenzeneazoformanilide being a hydroxy-derivative and not a quinone; the latter compound would have yielded a *s*-tribromo-derivative, the bromine atoms being in the aniline nucleus. The behaviour with benzenesulphinic acid is also in harmony with this view, since an additive compound is formed which is decomposed even by cold alkali hydroxides into its components, and therefore has the constitution $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{SO}_2\text{Ph})\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$; it forms colourless needles melting and decomposing at 166—167°. An isomeride, $\text{SO}_2\text{Ph}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{N}:\text{N}\cdot\text{CO}\cdot\text{NHPh}$, is produced when 2:4-dihydroxydiphenylsulphone is oxidised and then treated with phenylsemicarbazide in alcoholic solution; it crystallises in yellowish-brown needles melting and decomposing at 195—196°.

Quinonecarbamie hydrazone (*p*-hydroxybenzeneazoforamide),



is prepared by the action of semicarbazide on quinone at 0°, and crystallises in yellow needles decomposing at 178°.

4-Hydroxy-3:5-dibromobenzeneazoforamide,

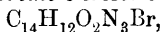


forms yellow needles melting and decomposing at 225°, dissolves in alkali hydroxides with a yellow coloration, and is decomposed on heating, 2:6-dibromophenol being produced.

p-Ethoxybenzeneazoformanilide, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{CO}\cdot\text{NHPh}$, is prepared either by ethylating *p*-hydroxybenzeneazoformanilide or by condensing *p*-ethoxyphenylhydrazine with phenylcarbimide and oxidising the product, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$ (crystallising in needles melting at 137—138°), with chromic acid; it forms red plates melting at 139—140°, and is reduced by phenylhydrazine. Both semicarbazide and phenylsemicarbazide effect the elimination of the ethoxy-group and convert it into the compound above mentioned. With benzenesulphinic acid, the additive product, crystallising in white needles and melting and decomposing at 180°, is obtained. *Carbamino-p*-ethoxyphenylhydrazide, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{H}_2\cdot\text{CO}\cdot\text{NH}_2$, prepared from *p*-ethoxyphenylhydrazine and potassium cyanate, crystallises in colourless leaflets which redden in the air and melt and decompose at 190°, and when oxidised by chromic acid are converted into *p*-ethoxybenzeneazoforamide, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{CO}\cdot\text{NH}_2$, which forms orange-red crystals melting and decomposing at 164—165°.

p-Benzoxybenzeneazoforamide, $\text{OBz}\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{CO}\cdot\text{NH}_2$, crystallises in orange-red leaflets, melting and decomposing at 191°. Although reduced by phenylhydrazine, it is not acted on by semicarbazide and is less reactive than the corresponding ethoxy-compound. *p*-Benzoxybenzeneazoformanilide forms yellow leaflets melting at 168—169°, dissolves in sulphuric acid with a red coloration, and yields a colourless additive product with benzenesulphinic acid, which softens at 140°, and is decomposed at 185°. When the *p*-benzoxy-compound is reduced by phenylhydrazine or zinc dust and acetic acid, the benzoate of phenylcarbamino-*p*-hydroxyphenylhydrazide, $\text{OBz}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{H}_4\cdot\text{CO}\cdot\text{NHPh}$, is obtained as colourless crystals melting at 203—204°.

Although it was possible that toluquinone and phenylsemicarbazide hydrochloride should react giving two isomerides, only one, *o*-cresol-5-azoformanilide, $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{N}:\text{N}\cdot\text{CO}\cdot\text{NHPh}$, is obtained as dark red crystals melting and decomposing at $198-199^\circ$. Since it only yields a monobromo-derivative, 3-bromo-*o*-cresol-5-azoformanilide,



a yellow, crystalline precipitate melting at $212-213^\circ$, which can also be obtained by condensation of phenylsemicarbazide with 5-bromo-toluquinone, these substances have the constitution here ascribed to them. The azocresol combines with phenylsemicarbazide, yielding the toluquinonediphenylsemicarbazone, $\text{C}_{21}\text{H}_{20}\text{O}_2\text{N}_6$, which is a red, crystalline powder decomposing at 246° . The additive compound with benzenesulphinic acid, $\text{C}_{20}\text{H}_{19}\text{O}_4\text{N}_3\text{S}$, is colourless, melts and decomposes at $153-154^\circ$, and is easily decomposed by alkali hydroxides. The benzoyl derivative, $\text{OBz}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{N}:\text{N}\cdot\text{CO}\cdot\text{NHPh}$, forms reddish-yellow prisms melting and decomposing at 150° .

Thymoquinone and phenylsemicarbazide yield the single azoformanilide,

$\text{OH}\cdot\text{C}_6\text{H}_3\text{MePr}^\beta\cdot\text{N}:\text{N}\cdot\text{CO}\cdot\text{NHPh}$ [$\text{Me}:\text{Pr}^\beta:(\text{OH}):\text{N}_2=1:4:3:6$], which crystallises in dark yellow needles melting at $179-180^\circ$ and behaves in an analogous manner to the corresponding benzene and toluene derivatives. It combines with phenylsemicarbazide, forming thymoquinonediphenyldisemicarbazide, $\text{C}_{24}\text{H}_{26}\text{O}_2\text{N}_6$, a dark yellow, crystalline powder decomposing at 242° , and with benzenesulphinic acid yields an additive product, $\text{C}_{23}\text{H}_{25}\text{O}_4\text{N}_3\text{S}$, which decomposes at $125-130^\circ$. When brominated in acetic acid solution in the presence of sodium acetate, a monobromo-derivative, $\text{C}_{17}\text{H}_{18}\text{O}_2\text{N}_3\text{Br}$, is obtained, crystallising in yellow needles melting at 203° ; it is also prepared from 6-bromothymoquinone and phenylsemicarbazide.

α -Naphthaquinone and phenylsemicarbazide yield the slightly soluble 1-hydroxynaphthalene-4-azoformanilide, $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}:\text{N}\cdot\text{CO}\cdot\text{NHPh}$, crystallising in greenish-yellow needles melting and decomposing at 235° . Its *p*-ethoxy-derivative, $\text{OEt}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}:\text{N}\cdot\text{CO}\cdot\text{NHPh}$, forms yellowish-white needles melting at 238° , and its benzoyl derivative yellow needles melting and decomposing at 230° . On bromination, the hydroxy-derivative yields 2-bromo-1-hydroxynaphthalene-4-azoformanilide, which crystallises in yellow needles melting and decomposing at 250° and is identical with the material prepared from bromonaphthaquinone.

β -Naphthaquinonephenylsemicarbazone is a red, insoluble, crystalline powder melting at $250-251^\circ$.

From the results of the investigation, the conclusions are drawn that the condensation products of quinones and carbamic hydrazides are not quinonehydrazones, but *p*-hydroxyazo-derivatives: that the tendency of hydroxyazo-derivatives is not to pass into hydrazones, but in the reverse direction: that the azoformanilide compounds herein described possess in a higher degree than other hydroxyazo-derivatives the power of behaving as quinone derivatives, thereby demonstrating the influence of the group combined with the azo-group. K. J. P. O.

s-Dibenzoylhydrazide and Azodibenzoyl. ERNST MOHR (*J. pr. Chem.*, 1904, [ii], 70, 281-302).—*s*-Dibenzoylhydrazide is

oxidised to benzoic acid and nitrogen by calcium hypochlorite, potassium or sodium hypobromite, or potassium tri-iodide, ferricyanide, or permanganate, in aqueous solution in presence of an excess of an alkali hydroxide. Azodibenzoyl, benzoic acid, and nitrogen are formed by oxidation of *s*-dibenzoylhydrazide with potassium tri-iodide, a faintly alkaline hypobromite, or acidified calcium hypochlorite in presence of a limited amount of alkali hydroxide, or with potassium ferricyanide or permanganate in presence of a limited quantity of alkali hydroxide and of ether.

Azodibenzoyl (Stollé and Benrath, *Abstr.*, 1900, i, 531; this vol., i, 935) is reduced when heated with benzaldehyde at 125—135° to *s*-dibenzoylhydrazide.

Tribenzoylhydrazide yields *s*-dibenzoylhydrazide when treated with dilute aqueous hydroxides, and is easily oxidised therefore by alkaline potassium permanganate, tri-iodide, or ferricyanide.

s-Benzoylphenylhydrazine is oxidised to phenylazobenzoyl by the action of iodine and sodium hydroxide solution on its ethereal solution.

G. Y.

Crystallographic Properties of *s*-Dibenzoylhydrazide and of Benzamide. ERNST MOHR (*J. pr. Chem.*, 1904, [ii], 70, 303—312).—*s*-Dibenzoylhydrazide crystallises from its hot saturated solution principally in slender needles, but also in monoclinic prisms. The amount of the monoclinic form is increased if a cold saturated solution is allowed to evaporate whilst cooled, and it is obtained free from the needles if an aqueous solution of the sodium derivative of *s*-dibenzoylhydrazide is left in a test-tube closed by a plug of cotton-wool. Both forms melt at 237—239°. If a suspension of both crystalline forms in alcohol is shaken for 3 days at 25°, the monoclinic crystals are converted into the needles. The needles are not converted into the monoclinic prisms when allowed to remain in contact with an excess of the latter in alcoholic suspension at 25° for 14 days or at 10—25° for a year.

Contrary to Wöhler and Liebig's statement (*Annalen*, 1832, 3, 270), aqueous solutions of benzamide deposit, on cooling, always triclinic (?) needles which change into stable monoclinic plates the more rapidly the higher the temperature of deposition. Solutions of benzamide in benzene, toluene, or xylene show the same behaviour. Triclinic (?) benzamide changes into the monoclinic form at 0°; the residue from an aqueous solution, when evaporated in a current of hydrogen at 97—98°, consists of monoclinic benzamide. Both crystalline forms of benzamide melt at 126—128°. When benzamide is heated at 135—140° in a sealed capillary tube, the small drops of molten substance crystallise, on cooling, in needles which in the course of some weeks change into monoclinic plates.

G. Y.

2:4:6-Trichloropyrimidine. SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1904, 37, 3657—3658).—A more convenient method of obtaining trichloropyrimidine than previously described (*Abstr.*, 1901, i, 168) consists in digesting barbituric acid with phosphorus oxychloride at 130—140°, distilling the mass in a vacuum at 190°, and

subsequently fractionally distilling. In this way, about 80 per cent. of the theoretical quantity is obtained.

E. F. A.

2 Methylpyrimidine. SIEGMUND GABRIEL (*Ber.*, 1904, 37, 3638—3643. Compare Abstr., 1902, i, 498).—6-*Hydroxy-2-methylpyrimidine*, $\text{CMe} \begin{smallmatrix} \text{N} \cdot \text{CH} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} \text{CH}$, prepared by the condensation of acetamide with ethyl formylacetate, crystallises from benzene in bundles of needles melting at 212° or from water with $1\frac{1}{2}\text{H}_2\text{O}$ in glistening, rhombic plates; the *hydrochloride* forms colourless needles, the *silver* salt a colourless, amorphous powder soluble in ammonia, and the *platinichloride* crystallises in octahedra. 6-*Chloro-2-methylpyrimidine*, formed by the action of phosphorus oxychloride on the foregoing compound, boils at 168° under 768 mm. pressure and crystallises in colourless rhombs melting at $59\text{--}60^\circ$. Ammonia in alcoholic solution converts it into 6-*amino-2-methylpyrimidine*, crystallising from acetone in colourless rhombs melting at 205° and forming a *nitrate*, which crystallises in prisms and melts and decomposes at $213\text{--}214^\circ$, an *aurichloride* crystallising in needles which melt and decompose at 203° , and a *platinichloride* melting and decomposing at $248\text{--}250^\circ$. It is reduced by zinc dust to 2-*methylpyrimidine*, $\text{CMe} \begin{smallmatrix} \text{N} \cdot \text{CH} \\ \text{N} \cdot \text{CH} \end{smallmatrix} \text{CH}$, which boils at 138° under 758 mm. pressure, melts at $-4\text{--}5^\circ$, and forms a *hydrochloride* crystallising in flat needles or rhombic plates, a *picrate* crystallising in yellow needles which sinter at 97° and melt at $106\text{--}107^\circ$, a *platinichloride* crystallising in short, yellow rods, and an *aurichloride* which crystallises in pointed needles melting at 124° .

E. F. A.

Quinazoline. II. SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1904, 37, 3643—3656. Compare Abstr., 1903, i, 445).—Quinazoline is best prepared by reduction of *o*-nitrobenzylamine with hydrogen iodide and red phosphorus to 2-aminobenzylamine, combination of this with formic acid to form dihydroquinazoline, and subsequent oxidation to quinazoline,

$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH} \cdot \text{N} \\ \text{N} = \text{CH} \end{smallmatrix}$. In a similar manner, *o*-nitrobenzylmethylamine can

be reduced to *o*-aminobenzylmethylamine, and this combined with formic

acid to yield 3-*methyl*dihydroquinazoline, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{NMe} \\ \text{N} = \text{CH} \end{smallmatrix}$, which

crystallises in prisms sintering at 80° and melting at $91\text{--}92^\circ$, boils at 309° under 766 mm. pressure, and forms a *picrate* crystallising in silky, yellow needles melting at $193\text{--}194^\circ$, a *platinichloride* crystallising in brownish-yellow needles, and a crystalline *hydriodide*.

Quinazoline is oxidised by permanganate to *pyrimidine-5:6-dicarboxylic acid*, $\text{C}_4\text{N}_2\text{H}_2(\text{CO}_2\text{H})_2$, H_2O , which on heating becomes brown at 180° and melts and decomposes at 265° ; the *ammonium* salt crystallises in long needles, melting and decomposing at 215° ; the *copper* salt forms bright blue crystals and the *silver* salt a heavy, crystalline, sparingly soluble powder.

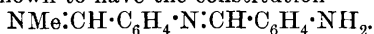
On distillation in a vacuum, pyrimidinedicarboxylic acid is converted

into *pyrimidine-5-carboxylic acid*, which crystallises in platelets sintering at 245° and melting at 270° to a dark red liquid.

Quinazoline combines with methyl iodide to form *quinazoline-3-methiodide*, a yellow, crystalline solid which, on heating, darkens at 115° , melts at 125 — 127° , and decomposes at 128° . On treatment with alkali, it is converted into *quinazoline-3-methylum hydroxide*,

$C_6H_4 \begin{smallmatrix} \text{CH:NMe}\cdot\text{OH} \\ \text{N=CH} \end{smallmatrix}$, which crystallises in rhombs melting at

163 — 165° to a brown liquid. On distillation with potassium hydroxide, an oil, $C_9H_{10}N_2$, and a base, $C_{15}H_{15}N_3$, were obtained. The oil is proved to be *o-aminobenzylidenemethylamine*, $NH_2\cdot C_6H_4\cdot CH:NMe$, and was prepared synthetically from *o-aminobenzaldehyde* and methylamine, whilst the base, which crystallises in rhombic plates melting at 188 — 190° , is shown to have the constitution



It forms a chrome-red *hydrochloride*, $C_{15}H_{15}N_3\cdot 2HCl$.

E. F. A.

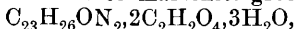
Constitution of the Rosaniline Salts and the Mechanism of their Formation. JULES SCHMIDLIN (*Compt. rend.*, 1904, 139, 602—604. Compare this vol., i, 698, 786, 943, 944).—When rosaniline-carbinol dissolves in dilute acetic acid, there is a development of heat and the formation of a colourless liquid, followed by an absorption of heat and the formation of a coloured liquid. In explanation of these phenomena, the author suggests that in the first stage a triazine ring is formed by the migration of the hydrogen atoms from one amino-group to the other two and the subsequent linking of the nitrogen atoms; at the same time, the interior benzene ring becomes saturated by absorbing three mols. of water, and the unstable colourless liquid is therefore a tetrahydroxycyclohexanerosaniline salt having the con-

stitution $HClN \begin{smallmatrix} \text{NH}_3\cdot C_6H_4 \\ \text{C(OH)} \begin{smallmatrix} \text{CH}_2\cdot\text{CH(OH)} \\ \text{CH}_2\cdot\text{CH(OH)} \end{smallmatrix} \text{CH} \begin{smallmatrix} \text{NH}_3\cdot C_6H_4 \\ \text{C}\cdot\text{OH} \end{smallmatrix} \end{smallmatrix}$; in the second

stage, the hexahydrobenzene ring, which is unstable under the influence of the triazine ring, loses $4H_2O$, and the coloured compound has

the quinonoid structure $ClN \begin{smallmatrix} \text{NH}_3\cdot C_6H_4 \\ \text{C} \begin{smallmatrix} \text{CH:CH} \\ \text{CH:CH} \end{smallmatrix} \text{C}=\text{C} \\ \text{NH}_3\cdot C_6H_4 \end{smallmatrix}$. M. A. W.

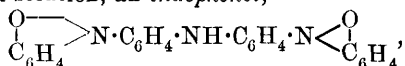
The Tetrahydroxycyclohexanerosanilines. JULES SCHMIDLIN (*Compt. rend.*, 1904, 139, 676. Compare this vol., i, 698, 785, 943, 944).—The colourless oxalate of malachite-green,



described by Lambrecht and Weil (compare this vol., i, 877), loses $4H_2O$ at 70° and becomes the coloured oxalate of malachite-green, $C_{23}H_{24}N_2\cdot 2C_2H_2O_4$; these facts afford a further confirmation of the quinonoid constitution of the coloured rosaniline salts. M. A. W.

[**Hydroxyphenyl Derivatives of 4:4'-Diaminodiphenylamine.**] FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 153130 and 153994).—On oxidising a mixture of 1 mol. of 4:4'-diamino-

diphenylamine, and 2 mols. of phenol with sodium dichromate in hydrochloric acid solution, an *indophenol*,



is obtained. Alcoholic sodium sulphide reduces it to *di-p-hydroxyphenyl-4:4'-diaminodiphenylamine*, $\text{NH}(\text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH})_2$, forming colourless leaflets melting at 208° , and dissolving readily in alcohol, sparingly in benzene.

When 1 mol. of phenol is employed, an *indophenol* is also obtained, yielding on reduction *p-hydroxyphenyl-4:4'-diaminodiphenylamine*, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, crystallising from water and melting at 185° . Hydrochloric acid and sodium hydroxide dissolve it to colourless solutions, the alkaline solution becoming blue in air.

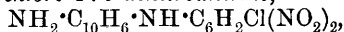
Both the indophenols and their reduction products yield blue dyes on fusion with sulphur and sodium sulphide. C. H. D.

[Action of Sulphur on Tolylenedicarbamide.] FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 153916).—On fusing tolylenedicarbamide (prepared from 1-tolylene-2:4-diamine and potassium cyanate) with sulphur at $200\text{--}230^\circ$, an orange dye is obtained, dissolving in hot solutions of alkali sulphides or in concentrated sodium hydroxide. C. H. D.

2:4:2':4'-Tetra-aminostilbene. RICHARD ESCALES (*Ber.*, 1904, 37, 3598—3600).—2:4:2':4'-Tetranitrostilbene, prepared by Krasusky's method (*J. Russ. Phys. Chem. Soc.*, 1895, 27, 335), may be reduced in glacial acetic acid solution by means of stannous chloride, the temperature rising to $60\text{--}80^\circ$. The orange solution of the tin salt is rendered alkaline with dilute sodium hydroxide and extracted with ethyl acetate, the upper layer then being distilled in a yellow glass flask in a current of carbon dioxide. 2:4:2':4'-Tetra-amino-stilbene, $\text{C}_{14}\text{H}_{16}\text{N}_4$, separates from amyl alcohol in an atmosphere of carbon dioxide in microscopic, brown crystals and melts at about 191° . Its solutions readily darken in air or light. The *hydrochloride* may be precipitated by hydrogen chloride. C. H. D.

Fluorindines of the Naphthalene Series. RUDOLF NIETZKI and AUGUST VOLLENBRUCK (*Ber.*, 1904, 37, 3887—3891).—The method of Nietzki and Slaboszewicz (*Abstr.*, 1902, i, 125) for the synthesis of fluorindines may also be applied to naphthalene derivatives.

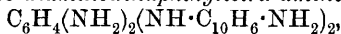
Aminonaphthyl-3-chloro-4:6-dinitroaniline,



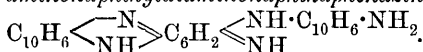
prepared by boiling $\alpha\beta$ -naphthylenediamine with dichlorodinitrobenzene and sodium acetate, forms brownish-red leaflets melting at 232° and dissolves sparingly in alcohol, readily in amyl alcohol or xylene. The *acetyl* derivative forms bright yellow needles and dissolves only in nitrobenzene. Boiling with amyl alcohol and sodium carbonate forms *diamindinaphthyl-dinitro-m-phenylenediamine*,



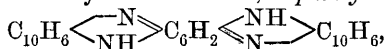
crystallising from pyridine and melting at about 300°. Stannous chloride reduces it to *diaminodinaphthyltetra-aminobenzene*,



which is readily oxidised by air or ferric chloride, forming the orange *hydrochloride* of *aminonaphthylldiaminonaphthaphenazine*,

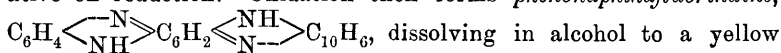


On heating with dilute hydrochloric acid, *naphthafluorindine*,



is obtained. The base forms red solutions; its salts are sparingly soluble, and form blue solutions. The solution in concentrated sulphuric acid is blue and non-fluorescent.

Aminonaphthylaminophenyldinitro-m-phenylenediamine, prepared from aminonaphthylchlorodinitroaniline and *o*-phenylenediamine, crystallises in leaflets, melts at 259°, and yields a *tetra-aminobenzene* derivative on reduction. Oxidation then forms *phenonaphthafluorindine*,



dissolving in alcohol to a yellow solution with red fluorescence. The hydrochloride forms a blue solution. C. H. D.

Tetra-aminocarbazole. RICHARD ESCALES [and K. WOLGAST] (*Ber.*, 1904, 37, 3596—3598).—Ciamician and Silber have shown (*Abstr.*, 1882, 1103) that four isomeric tetranitrocarbazoles are produced in the action of nitric acid on carbazole. The authors describe the separation of the isomerides, and obtain considerably lower melting points than Ciamician and Silber (α , 285—286°; β , 273°; γ , 275°; the δ -compound was not obtained in a crystalline form: C. & S. gave α , 308°; β , 320°; and γ , 275°).

Stannous chloride reduces the ice-cold solutions of the tetranitro-compounds in glacial acetic acid, and after decomposing the tin salt with hydrogen sulphide, filtering, and passing a current of hydrogen chloride through the filtrate, the *hydrochloride* of the corresponding *tetra-aminocarbazole*, $\text{C}_{12}\text{H}_{13}\text{N}_5\cdot 4\text{HCl}$, is obtained. The α -, β -, and γ -hydrochlorides crystallise from dilute alcohol on the addition of ether in greyish-white needles; the δ -compound forms yellow crystals.

C. H. D.

[*p*-Diazonium Compounds of Phenylalkylnitrosoamines.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 154336).—*p*-Aminoalkylanilines (1 mol.) react with sodium nitrite (2 mols.) to form the *p*-diazonium compounds of the corresponding phenylalkylnitrosoamines, which readily combine with 1:8-dihydroxynaphthalene-3:6-disulphonic acid in alkaline or acetic acid solution, forming violet azo-dyes. On hydrolysing with warm dilute acids, the nitroso-group is removed, and blue azo-dyes are obtained, identical with those prepared from 1:8-dihydroxynaphthalene-3:6-disulphonic acid and diazotised *p*-aminoalkylanilines.

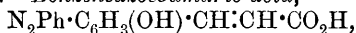
C. H. D.

Azo-dyes from Ethers of Diaminocresol and Chlorodiaminophenol. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 153939 and 153940).—A blue azo-dye is obtained by diazotising an ether of 2-acylamino-5-amino-*p*-cresol, combining with the sulphonic acids of 1:8-dihydroxynaphthalene, and removing the acyl group from the products; or by diazotising an ether of 5-nitro-2-amino-*p*-cresol, combining with the same acids, and reducing the products.

Similar dyes are obtained in the same way from ethers of 4-chloro-5-amino-2-acylamino-phenol or 4-chloro-5-nitro-2-aminophenol.

The introduction of an alkyloxy-group in this way has the same effect in the production of a blue shade as the alkylation of the amino-group. C. H. D.

Influence of Unsaturated Side-chains on the tendency of Phenols to Couple, and the Colour of the resulting Oxyazo-compounds. WALTHER BORSCHÉ and F. STREITBERGER (*Ber.*, 1904, 387, 4116—4136).—*Benzeneazocoumaric acid*,

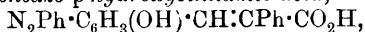


prepared from *o*-coumaric acid and phenyldiazonium chloride, is a brownish-red, crystalline powder melting and decomposing at 206°; the *acetate* crystallises in yellow plates, melting at 167—169°. *Sulphobenzeneazocoumaric acid* forms a red powder which could not be melted in a sulphuric acid bath. *Sulphobenzeneazocoumarin*, prepared by the interaction of coumarin and diazobenzenesulphonic acid, separates from hot water in reddish-yellow needles. *Benzeneazo-m-hydroxycinnamic acid* forms bright red crystals grouped in stars which melt at 168°. The corresponding compound of *m*-hydroxycinnamic acid and diazobenzenesulphonic acid could not be isolated; similarly, with *p*-hydroxycinnamic acid, only undefinable decomposition products were obtained.

Benzeneazomelilotic acid, $\text{N}_2\text{Ph}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, crystallises from dilute alcohol in bright yellow plates melting at 130°. *Disbenzeneazomelilotic acid*, $\text{OH}\cdot\text{C}_6\text{H}_2(\text{N}_2\text{Ph})_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, crystallises from alcohol in dark brown plates melting at 194°. *Sulphobenzeneazomelilotic acid*, prepared by coupling melilotic acid with diazotised sulphanilic acid, crystallises from dilute hydrochloric acid in dark red needles. *Benzeneazo-m-hydroxydihydrocinnamic acid*, $\text{N}_2\text{Ph}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, separates in yellowish-red, silky, glistening needles which melt at 146°. *Disbenzeneazo-m-hydroxydihydrocinnamic acid* is a brown, crystalline powder melting at 179—180°; *sulphobenzeneazo-m-hydroxydihydrocinnamic acid* separates as a dark red, crystalline powder. *Benzeneazo-p-hydroxydihydrocinnamic acid* crystallises in red needles which melt at 140—141°; the corresponding *sulphonic acid* derivative is a dark red powder.

α-Phenylbenzeneazocoumarin crystallises from acetic acid in reddish-brown needles, from alcohol in orange-yellow plates which melt at 205°; the corresponding *sulphonic acid* also forms orange-yellow needles. *α-Phenyl-m-hydroxycinnamic acid* could not be brought to enter into reaction with diazo-compounds; the corresponding *para*-compound

forms *α-phenylbenzeneazo-p-hydroxycinnamic acid*,



which crystallises in yellow needles melting at 247°. No corresponding compound was obtained with *p*-diazobenzenesulphonic acid.

α-Phenylbenzeneazomelilotic acid, prepared from *α*-phenylmelilotic acid and a solution of a diazo-compound, crystallises in aggregates of yellowish-red needles melting at 152—153°; the *disbenzeneazo*-compound forms a dark brown, crystalline mass melting at 223°; the *benzenesulphonic acid* derivative is dark red. *α-Phenylbenzeneazo-m-hydroxydihydrocinnamic acid* crystallises from alcohol in reddish-yellow, star-shaped needles melting at 177°. The corresponding *p-hydroxy*-compound forms yellowish-red plates melting at 159°. *Benzenaezo-eugenol* crystallises in long, dark red needles melting at 76—77°, easily soluble in dilute alkaline hydroxides with a bluish-red coloration; *benzeneazoiso-eugenol* is a brown, amorphous powder. E. F. A.

Diazo-compounds from Amino-*α*-naphtholdisulphonic Acid. KALLE & Co. (D.R.-P. 153299).—On nitrating and reducing 2:6-dichlorobenzenesulphonic acid, an aminosulphonic acid is obtained the diazo-derivative of which combines with 8-amino-*α*-naphthol-3:6-disulphonic acid. The aminoazo-dyes thus obtained then combine readily with diazotised amines, yielding fast diazo-colouring matters. C. H. D.

Substituted Derivatives of Phenyldiazoaminobenzene. LÉO VIGNON and ADOLPHE SIMONET (*Compt. rend.*, 1904, 139, 569–571. Compare this vol., i, 637).—The following substituted derivatives of phenyldiazoaminobenzene are readily prepared by the action of diphenylamine on the corresponding substituted diazotised amine: *o*-, *m*-, and *p*-nitrophenyldiazoaminobenzenes are soluble in alcohol, ether, or benzene, insoluble in water, the first two are liquids, the third a red solid, melting at 63°; *o*- and *m*-chlorophenyldiazoaminobenzenes are liquids, whilst the *p*-compound melts at 20°; 2:4-dichlorophenyl-1-diazoaminobenzene is an orange-yellow solid melting at 35—40°; 1:3:5-trichlorophenyl-2-diazoaminobenzene is a brown solid melting at 38—39°; *o*-, *m*-, and *p*-bromophenyldiazoaminobenzenes are unstable liquids; 1:3-dibromophenyldiazoaminobenzene is a red solid melting at 80°; 1:3:5-tribromophenyldiazoaminobenzene is a yellow, crystalline solid melting at 48°; *p*-iodophenyldiazoaminobenzene is a deep red liquid; 2:4-di-iodophenyldiazoaminobenzene is a brown solid melting at 70°; *o*-methoxyphenyldiazoaminobenzene is a brown, crystalline solid melting at 30—32°; the corresponding para-derivative is a reddish-brown liquid. M. A. W.

The Combination of Nitrogen in Proteids. C. H. ROTHERA (*Beitr. chem. Physiol. Path.*, 1904, 5, 442—448. Compare Gümbel, this vol., i, 460).—From experiments made by Embden and also by the author it appears that only some 2/3 of the total amide nitrogen is driven off as ammonia when the distillation with magnesia is conducted in a vacuum at 40°; the remaining 1/3 is given off at higher temperatures.

When the acid decomposition of proteids is carried out in presence of reducing agents, for example, hydriodic acid or stannous chloride (compare Hlasiwetz and Habermann, *Annalen*, 1873, 169, 150), the amount of monamino-nitrogen is increased, and that of the diamino-nitrogen diminished.

The values obtained for the nitrogen in serum albumin are: amide, 1.04; melanin, 0.26; monoamino-, 9.98; diamino-, 5.21 per cent. (compare Gumbel).

For ichthyn from the eggs of *Torpedo marmorata*, the following numbers were found: total nitrogen, 15.7; amide, 1.32; melanin, 0.198; monoamino-, 9.58; diamino-, 3.99 per cent. These numbers differ slightly from those obtained for ichthyn from the sturgeon.
J. J. S.

Hydrolysis of Proteids. EMIL FISCHER and EMIL ABDERHALDEN (*Zeit. physiol. Chem.*, 1904, 42, 540—544).—The tyrosine obtained by the hydrolysis of casein (Abstr., 1901, i, 780) is highly impure and can only be obtained pure after repeated crystallisations from water. Two impurities which have been isolated are lysine and a *diamino-trihydroxydodecanoic acid*, $C_{12}H_{26}O_5N_2$, both of which are more readily soluble in water than tyrosine. The new acid is isolated from the mother liquors by precipitation with phosphotungstic acid, and is purified by means of the *hydrochloride*, which crystallises from concentrated hydrochloric acid in slender needles. The acid turns brown, melts, and decomposes at about 255°; it is optically active, $[\alpha] - 9^\circ$, and is readily soluble in dilute mineral acids. The *copper* salt, $C_{12}H_{24}O_5N_2Cu$, crystallises in pale blue plates. The yield of acid depends to a large extent on the details of the method of hydrolysis.

Serin has been detected among the products formed by the hydrolysis of gelatin with acids.
J. J. S.

Proteids of Wheat Gluten. I. Proteids of Wheat Meal. JOSEF KÖNIG and P. RINTELEN (*Zeit. Nahr. Genussm.*, 1904, 8, 401—407).—Fresh gluten (2—3 kilos.), well washed with water, was made into threads by means of a meat press and treated successively with absolute alcohol and ether to remove water and fat. The small amount of proteid dissolved by the alcohol was recovered by precipitating with ether, and after being treated with alcohol-ether was added to the rest. The whole was then put into a long linen bag and suspended in a cylinder containing 65 per cent. alcohol which was frequently renewed. Finally, the bag was gently pressed. The clear extract was mixed with 97 per cent. alcohol (about 6.25 litres to 2.5 litres of extract) so as to raise the strength to 85—90 per cent., and the whole immersed in ice-water. The precipitate obtained in this manner, consisting of gliadin and mucedin, is again dissolved in 65 per cent. alcohol, half of which is distilled off. On cooling, the gliadin separates, adhering to the flask. The alcohol is poured off, and distilled until two-thirds remain and allowed to cool. The precipitate thus obtained is neglected, being possibly a mixture of gliadin and mucedin. The filtrate from it, evaporated to dryness, yielded a considerable amount of pure mucedin.

The first filtrate (from the gliadin and mucedin) contained the

gluten-fibrin. This is obtained by distilling off the alcohol and extracting the residue with water, drying, and extracting with ether. It is then dissolved in alcohol containing a little potassium hydroxide, shaken several times with ether, the slightly alkaline solution exactly neutralised with hydrochloric acid, and evaporated to dryness. This treatment is necessary to remove completely the sugar and fat.

The average composition of the products was found to be as follows :

| | C. | H. | N. | S. | O. |
|-----------------------|-------|------|-------|------|-------|
| 1. Gluten-fibrin..... | 55.30 | 8.17 | 16.86 | 1.07 | 19.73 |
| 2. Gliadin | 52.70 | 7.62 | 17.77 | 0.95 | 20.96 |
| 3. Mucedin | 53.33 | 8.07 | 16.83 | 0.78 | 20.99 |

The three substances dissolve respectively in 88—90, 60—70, and 30—40 per cent. alcohol.

N. H. J. M.

Decomposition of Pseudomucin by Concentrated Boiling Acids. I. J. OTORI (*Zeit. physiol. Chem.*, 1904, 42, 453—460).—Pseudomucin (Steudel, Abstr., 1902, i, 399) containing some 2.22 per cent. of ash was heated on the water-bath with 33.3 per cent. sulphuric acid and the mixture ultimately boiled during 12 hours. On dilution, only a small amount of humin substance was precipitated. The filtrate was extracted with ether in a Kutscher-Steudel extractor and the ethereal solution tested for acids. The sulphuric acid solution was examined for bases. The following is a complete list of the substances isolated: ammonia, 0.7517; guanidine, 0.0393; arginine, 0.2875; lysine, 2.6389; tyrosine, 1.089; leucine, 4.677; oxalic acid, 0.1275; lævulic acid, 1.971; a reducing sugar calculated as dextrose, 0.7333; and humin, 6.056 per cent.

J. J. S.

Lecithin. RICHARD WILLSTÄTTER and KARL LÜDECKE (*Ber.*, 1904, 37, 3753—3758. Compare Ulpiani, Abstr., 1901, i, 491, 498).—The hydrolysis of lecithin with cold barium hydroxide solution gives an optically active glycerophosphoric acid which probably has the formula $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OPO}_3\text{H}_2$; lecithin thus appears to have the constitution attributed to it by Ulpiani. It is not decided whether Pelouze's glycerophosphoric acid, to which the same formula has been given, is the racemic form of the active acid obtained from lecithin.

Barium glycerophosphate from lecithin, $\text{C}_3\text{H}_7\text{O}_6\text{P}\cdot\text{Ba}, \frac{1}{2}\text{H}_2\text{O}$, is precipitated from its aqueous solution on adding alcohol as a flocculent mass; different values of $[\alpha]_D$ varying from -0.68° to -1.712° were observed. The corresponding *calcium* salt forms small needles, has the composition $\text{C}_3\text{H}_7\text{O}_6\text{P}\cdot\text{Ca}, \frac{3}{4}\text{H}_2\text{O}$, and $[\alpha]_D -0.68^\circ$ to -2.09° . The barium salt of the synthetical acid separates with H_2O , but is not crystalline; the calcium salt of the same acid forms small needles with $1\frac{1}{2}\text{H}_2\text{O}$. The calcium salt of the natural acid has a solubility of 2.62 grams per 100 c.c. of saturated solution at 18° , the solubility of the analogous synthetic salt being 5.54.

W. A. D.

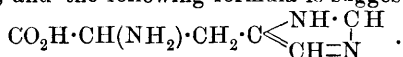
Blood Pigments. P. P. LAIDLAW (*J. Physiol.*, 1904, 31, 464—472).—Hoppe-Seyler showed that the removal of iron from hæmatin in the absence of reducing agents is difficult. This was denied by

Nencki and Sieber. The present experiments show that the addition of mineral acids (except concentrated sulphuric acid) to oxyhæmoglobin produces hæmatin, but to hæmoglobin produces hæmatoporphyrin. In the absence of oxygen, even 2 per cent. hydrochloric acid produces hæmatoporphyrin with an intermediate formation of hæmochromogen; in the presence of oxygen, the concentrated acid, aided by heat and pressure, is necessary. Oxygen confers stability on the iron of the blood pigment. It further appears that the hæmatoporphyrin group is present as such in hæmoglobin, and hæmatoporphyrinuria becomes intelligible if it is considered that the body-cells deal with the reduced pigment. If hæmatoporphyrin is dissolved in dilute ammonia and warmed with Stokes's fluid and a little alkaline hydrazine hydrate, the iron is replaced, hæmochromogen reappears, and by shaking this with air, hæmatin presenting all the characters of the natural pigment is obtained. Hæmin crystals were, however, not readily obtained; this is true also for pure natural hæmatin: an important factor in crystal formation is the union with proteid, and it is probable that the acetyl introduced takes the place of the globin group. If hæmatoporphyrin, dissolved in ammonia, is boiled with cuprammonium solution, a pigment having all the characters of turacin is formed at once. A cobalt hæmatoporphyrin was also obtained. Bilirubin does not form an iron compound in this way, but it does yield one with copper; the solution is green in alkaline and purple in acid solution. This may be employed as a test for bilirubin.

W. D. H.

Constitution of Histidine. I. HERMANN PAULY (*Zeit. physiol. Chem.*, 1904, 42, 508—518. Compare Fränkel, Abstr., 1903, i, 650).—The presence of a carboxylic group in the histidine molecule has been confirmed by esterification with methyl alcohol and hydrochloric acid. The *methyl ester dihydrochloride*, $C_5H_8N_3 \cdot CO_2Me \cdot 2HCl$, crystallises from methyl alcohol in flat, rhombic prisms melting and decomposing at 196° and readily soluble in water. The free ester is a viscid oil. Fränkel has already proved the presence of an amino-group in the histidine molecule, and as it is now shown that histidine yields a dinaphthalene- β -sulphone derivative, an imino-group must also be present. The *disulphone*, $C_6H_7O_2N_3(SO_2 \cdot C_{10}H_7)_2$, crystallises from 60 per cent. alcohol in slender, felted needles which are insoluble in water.

Histidine reacts with diazobenzenesulphonic acid in the presence of alkali, yielding a dark cherry-red dye which turns orange-coloured when acidified. This is an extremely delicate reaction, and can be made use of in testing for histidine if tyrosine is known to be absent. None of the other hydrolytic products gives a similar reaction. All proteids which yield histidine and tyrosine on hydrolysis, for example, sturin, histon, edestin, and casein, give the red colour with diazobenzenesulphonic acid, whereas proteids which do not yield histidine and tyrosine on hydrolysis do not give the coloration. The stability of histidine towards acid oxidising agents (nitric acid) is used as an argument against Fränkel's formula, which contains a dihydropyrimidine ring, and the following formula is suggested:



This contains the iminazole ring, and the properties of histidine are in agreement therewith. J. J. S.

Constitution and Synthesis of Adrenaline. ERNST FRIEDMANN (*Beitr. chem. Physiol. Path.*, 1904, 6, 92—93).—Pauly (this vol., i, 128), discussing the constitution of adrenaline, describes it as a secondary base having the formula $C_6H_4(OH)_2 \cdot CH(OH) \cdot CH_2 \cdot NHMe$ or $C_6H_4(OH)_2 \cdot CH(NHMe) \cdot CH_2 \cdot OH$ [$CH : (OH)_2 = 1 : 3 : 4$]. The present research lends support to the first of the two suggestions, a view also taken by Jowett. The material used was von Fürth's adrenaline tribenzenesulphonate (*Abstr.*, 1903, i, 669), which is lævorotatory and contains a free aliphatic hydroxyl group; by oxidation, a substance is formed which contains the same number of carbon atoms, but no asymmetric carbon atom. This testifies to its ketonic character. By further oxidation, another substance is obtained also with the same number of carbon atoms, which is a substituted acid amide. The names and formulæ ascribed to the grouping in the two products are respectively *adrenalone*, $C_6H_4(OH)_2 \cdot CO \cdot CH_2 \cdot NHMe$, and *peradrenalone*, $C_6H_4(OH)_2 \cdot CO \cdot CO \cdot NHMe$. This is confirmed by the following attempt at synthesis. By the action of methylamine on chloracetylcatechol, a product is obtained, methylaminoacetylcatechol, which is adrenalone. The power of this synthetic adrenalone to elevate blood-pressure is very great. Further work is in progress. W. D. H.

Constitution and Synthesis of Adrenaline. HANS MEYER (*Centr. Physiol.*, 1904, 18, 501).—A claim for priority in favour of F. Stolz and W. Reser, who arrived at the same conclusions as Friedmann (see preceding abstract) by the same methods in July last.

W. D. H.

Amylase. JEAN EFFRONT (*Chem. Centr.*, 1904, ii, 767; from *Mon. Sci.*, [iv], 18, 561—565).—Asparagine acts only on the first products of the hydration of starch, and the further this has proceeded the less its influence. It does not act as an acid, and the diastatic activity is reduced by addition of acetic acid, whilst considerable amounts of asparagine act favourably. The conclusion is drawn that all amino-acids have a beneficial influence on amylase independent of temperature and degree of alkalinity. Aspartic acid has about the same effect as asparagine, whilst succinamide hinders the diastatic action.

Glycine, sarcosine, alanine, leucine, glutamic acid, hippuric acid, creatinine, and creatine all act favourably, as do also the products of the action of pepsin and trypsin on proteids. Liebig's extract has only a slight effect. N. H. J. M.

Researches on Lactase. A. BRACHIN (*J. Pharm. Chim.*, 1904, [vi], 20, 300—308).—Lactase is found to be present in various plants of the orders *Rosaceæ*, *Cruciferae*, *Cornaceæ*, and *Rutaceæ*, but was not found in the lower plants. Lactase (in two per cent. solution) ceases to be active at between 75° and 80°.

Acetic acid of the strength 2·4 per 1000 prevents the hydrolysis of lactose by lactase, whilst the hydrolysis of amygdalin by emulsin is not prevented by acid of the strength 12·0 per 1000. Sulphuric and oxalic acids of the strength 0·09 to 0·1 per 1000 and tartaric acid of the strength 7·5 per 1000 also prevent the action of lactase. G. D. L.

Studies on Enzyme Action. V. Hydrolysis of Isomeric Glucosides and Galactosides by Acids and Enzymes. E. FRANKLAND ARMSTRONG (*Proc. Roy. Soc.*, 1904, 74, 188—194. Compare this vol., i, 956, 957).—The hydrolysis of 3 per cent. solutions of α -methylglucoside, β -methylglucoside, α -methylgalactoside, β -methylgalactoside, and salicin by $N/2$ hydrochloric acid has been studied at 74·1° and 74·8°. The values of the velocity constant K at 74·1°, calculated on the assumption that the change is unimolecular, are as follow: α -methylglucoside, 0·0100; β -methylglucoside, 0·0179; α -methylgalactoside, 0·0542; β -methylgalactoside, 0·0884; salicin, 0·0601. The experiments on enzyme activity have so far been confined to the hydrolysis of maltose and α -methylglucoside at 22°. When these two are hydrolysed by the same yeast extract under precisely similar conditions, the initial value of K in the case of the glucoside lies at about 0·025, in the case of maltose about 0·12 or even higher. In each case, the value of K falls off as the hydrolysis proceeds, this feature being especially noticeable in the case of the maltose, where the influence of the products of change is more obvious. The above numbers show that the enzyme is much more active than the acid in promoting hydrolysis. It is probable, however, that the enzyme owes its apparent activity to its greater affinity for the sugar, and that in reality the acid has the greater hydrolytic activity. J. C. P.

Studies on Enzyme Action. VI. Sucroclastic Action of Acids as contrasted with that of Enzymes. Part II. E. FRANKLAND ARMSTRONG and ROBERT JOHN CALDWELL (*Proc. Roy. Soc.*, 1904, 74, 195—201. Compare this vol., i, 956, 957, and preceding abstract).—When solutions of sucrose containing 171 and 342 grams per litre are hydrolysed by $N/500$ HCl at 40°, the velocity constant K increases in value during the first 4 or 5 hours of the change and then remains constant. In the first period, the change proceeds at an approximately linear rate, thus completing the analogy between acid and enzyme action (compare *loc. cit.*, 956). In both cases, when the proportion of hydrolyst is relatively small, the change is at first approximately a linear function of the time and subsequently a logarithmic function; when the proportion of hydrolyst is larger, the change is a logarithmic function throughout, which may become modified by secondary causes.

The influence of the products of change on the rate of hydrolysis of sucrose has also been studied. It appears that about the same increase in the value of K is produced by molecular quantities of dextrose and lævulose, whilst the molecular effect of the biose sucrose is about twice the molecular effect of the monose. J. C. P.

The Hydrolysis of Optically Inactive Esters by means of Enzymes. I. **The Action of Lipase on Esters of Mandelic Acid. The Resolution of Inactive Mandelic Acid.** HENRY D. DAKIN (*J. Physiol.*, 1903, 30, 253—263. Compare Proc., 1903, 161).—Inactive methyl, ethyl, *iso*amyl, and benzyl mandelates are hydrolysed by lipase, the dextrorotatory component being more rapidly decomposed than the levorotatory component. A method of determining accurately the degree of hydrolysis and the optical activity of the product is described.

The results are best explained on the assumption that lipase is an asymmetric compound, and forms additive compounds with the ester. These compounds not being optical antipodes are hydrolysed with unequal velocities.

Lipase was found to be without action on *l*-menthyl or *d*-bornyl mandelate. Horse serum contains a lipolytic enzyme which readily hydrolyses ethyl mandelate, giving an active product, but no such result could be obtained with pig serum, although the organs of the pig furnish specially active lipase preparations.

*iso*Amyl mandelate forms a colourless oil boiling at 164—165° under 12 mm. pressure and solidifying on cooling. C. H. D.

Decomposition of Fats by Enzymes. SERGIUS FOKIN (*Chem. Rev. Fett. Ind.*, 1904, 11, 91—92; 118—120; 139—141; 167—170; 193—195; 224—226; 244—247. Compare this vol., ii, 199, 280).—Castor oil seed was mixed with dilute sulphuric acid and almond oil, and the amount of fatty acid, produced at 25°, was estimated. Seeds from various sources, which had been kept for variable times, gave similar results.

The amount of water necessary depends on the amount of seed used. The concentration of mineral acid must be within $N/20$ and $N/120$, according as the amount of seed is between 5 and 40 per cent. With small amounts of mineral acids the process is slow, whilst with large amounts of a concentration greater than $N/10$ the action of the ferment is totally destroyed.

The percentage yield of fatty acid is increased by carefully mixing the mass, and is larger the more fat is used. Solid and rancid fats are decomposed with difficulty. The decomposition can be effected by carbonic acid or by fatty acids. The results obtained with various oils are represented by curves. The action of pancreas juice on almond oil was also examined. A. McK.

Ferment Action and Ferment Loss. H. REICHEL and KARL SPIRO (*Beitr. chem. Physiol. Path.*, 1904, 6, 68—86).—Experiments on the velocity of rennet action shows that the loss of activity which apparently occurs after previous action is due to inclusion of some of the ferment in the cheese and whey. There is no real loss of activity associated with previous action; in other words, rennet acts as a catalytic agent. W. D. H.

Yeast Ferments. K. SHIGA (*Zeit. physiol. Chem.*, 1904, 42, 502—507. Compare Milroy, Abstr., 1897, i, 232; Jones and Partridge, this vol., i, 838).—When guanine is added to yeast extract which is

undergoing autolysis in the presence of toluene, it is found that the base is destroyed, whereas the amount of xanthine increases. The amounts of adenine and hypoxanthine vary considerably in different experiments.

Kossel and Dakin's arginase is also present in yeast extract. This has been proved by the decomposition of arginine added to the extract.

J. J. S.

Isolation of Zymase from Animal and Vegetable Tissues. PIERRE MAZÉ (*Ann. Inst. Pasteur*, 1904, 18, 535—544. Compare Abstr, 1902, ii, 622).—A critical review of Stoklasa's work; his facts appear to be correct, but his explanation is disputed.

W. D. H.

Action of Phosphorus Chlorides on Organomagnesium Derivatives of the Aromatic Series. R. SAUVAGE (*Compt. rend.*, 1904, 139, 674—676. Compare Auger and Billy, this vol., i, 983).—Phosphorus oxychloride reacts readily at the ordinary temperature with organomagnesium derivatives of the aromatic series to form the corresponding triarylphosphine oxide, R_3PO , and the diarylphosphinic acid, $R_2PO\cdot OH$; the following compounds were thus prepared. (1) From magnesium phenyl bromide, *triphenylphosphine oxide*, soluble in alcohol, acetic acid, or benzene, and crystallising from a mixture of benzene and light petroleum in beautiful, white needles melting at 156° . (2) From magnesium benzyl chloride, *dibenzylphosphinic acid*, crystallising from acetic acid in white plates melting at 190 — 191° , and *tribenzylphosphine oxide*, crystallising from alcohol in needles melting at 217° . (3) From magnesium α -naphthyl bromide, *α -dinaphthylphosphinic acid*, crystallising in plates from acetic acid and melting at 220° , and *trinaphthylphosphine oxide*, not yet obtained in a state of purity owing to its insoluble nature. Phosphorus trichloride reacts with magnesium phenyl bromide with great energy, forming *triphenylphosphine*, which crystallises in large crystals from alcohol and melts at 79° .

M. A. W.

JOURNAL

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THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

PART II.

General and Physical Chemistry.

Critical Pressure of Luminescence of Gases. ALEXANDRE DE HEMPTINNE (*Bull. Acad. Roy. Belg.*, 1903, 851—863. Compare Abstr., 1902, ii, 58 ; 1903, ii, 193, 199).—The term “critical pressure of luminescence” is used synonymously with the term “Umkehrdruck” employed by Ebert (*Ann. Phys. Chem.*, 1899, [ii], 69, 372), and refers to that limiting pressure of a gas, the increase or decrease of which equally leads to greater electric resistance. The author has studied especially the influence of a magnetic field on the value of this “critical pressure,” using for this purpose a Tesla coil, terminating in two metallic plates, 20 cm. long and 7 cm. broad, between which the tubes containing the gas and connected to a McLeod gauge were placed. This arrangement eliminates the error due to change of distance between the electrodes observed by Ebert (*loc. cit.*). The “critical pressure” in a tube 6.5 cm. long and 1 cm. in diameter depends, under these conditions, on the positions of the tube relatively to those of the metallic plates, being greatest when the tube is vertical and parallel to the plates, and least when it is placed lengthwise and perpendicular to them. Under the additional influence of a magnetic field, the “critical pressure” is reduced in the former position (parallel to the lines of force) and increased in the second (perpendicular

to the lines of force). The author explains these effects induced by the magnetic field by assuming that the movement of each electrified particle of gas is then a resultant of its inherent movement as an electrified particle and that due to the magnetic field. This changes the range of movement of the particles in the first position of the tube from the diameter of the tube to a range intermediate between this and the whole length of the tube, and in the second position decreases the range of movement from that of the whole length of the tube to a range intermediate between this and the diameter of the tube. In conformity with this explanation, it was observed that no change in the "critical pressure of luminescence" occurs in a magnetic field when the gas is contained in a spherical vessel. T. A. H.

Luminous Effects at Electrodes and a New Spectroscopic Method. WERNER VON BOLTON (*Zeit. Elektrochem.*, 1903, 9, 913—922).—When a metallic rod connected with a current source giving an *E.M.F.* of 110 volts is dipped slowly into a quantity of sulphuric acid (1 : 20) or nitric acid (1 : 4) into which an anode connected with the positive pole of the source of current has already been placed, the end of the rod gives off a brilliant light which, when examined in the spectroscope, shows the lines of the metal employed together with the hydrogen spectrum.

The metallic spectra are also obtained when platinum wires are employed and a small quantity of a salt of the metal is added to the electrolyte, the best results being obtained with nitric acid. A carbon rod gives a continuous spectrum. At the anode, a very faint light is observed, the spectrum of which is mainly continuous. The metallic spectra observed at the cathode appear to be due to the vaporisation of the metals as they are deposited; the cathode is always surrounded by a film of hydrogen, through which the current passes in the form of minute sparks. The method is very sensitive; a solution of 1 mg. of strontium nitrate in 3 litres of water, for example, shows the strontium spectrum distinctly. Charts are given showing the spectra observed. T. E.

Relationship between Spectra and Atomic Weights. CARL RUNGE (*Phil. Mag.*, 1903, [vi], 6, 698—701. Compare Abstr., 1903, ii, 346).—An adverse criticism of Watts' method (Abstr., 1903, ii, 654) of calculating the atomic weight of radium from its spectrum.

J. C. P.

Absorption of Ultra-violet Rays in Ozone. EDGAR MEYER (*Ann. Physik.*, 1903, [iv], 12, 849—859).—The author has determined the value of the absorption coefficient over the range $\lambda = 185\mu\mu$ to $\lambda = 300\mu\mu$, and finds a minimum value at $\lambda = 205\mu\mu$, and a maximum at $\lambda = 258\mu\mu$. The latter agrees with the position ($\lambda = 256\mu\mu$) of the absorption band given by Hartley (Trans., 1881, 39, 60, 111).

The sun's spectrum comes more or less suddenly to an end at $\lambda = 293\mu\mu$, and the absorption of the solar radiation in the earth's atmosphere, which is responsible for that fact, is, according to Hartley,

due to the ozone. Taking into account the percentage of ozone in the atmosphere and the values of the absorption coefficient obtained by himself, the author regards Hartley's view as probably correct.

J. C. P.

Spectra of Neon, Krypton, and Xenon. EDWARD C. C. BALY (*Phil. Trans.*, 1903, A, 202, 183—242).—The gases were in all cases illuminated by the passage of an electric discharge through them under reduced pressure. The heating of the electrodes in presence of these monatomic gases is much more marked than in ordinary circumstances, and this heating effect is very troublesome in view of the large amount of hydrogen evolved from the electrode and the consequent masking of the spectrum to be investigated. The phenomenon of electrical evaporation, common enough with platinum and similar electrodes, has been observed for the first time with aluminium electrodes.

The spectra of the gases consist of bright, well-defined lines similar to those of argon and helium, the definition depending, however, on the pressure in the vacuum tube. If the pressure is not less than a certain small value, the appearance of the spectrum becomes confused, and at times it is almost continuous. The spectrum of neon consists of very bright lines in the orange and red regions, and its character is not materially altered by the introduction into the circuit of a Leyden jar and spark gap. Krypton and xenon, on the other hand, are like argon in possessing first and second spectra, according as (1) the direct discharge is passed, or (2) a Leyden jar and spark gap are introduced into the circuit. The first spectrum of krypton consists of a few lines, the most important being the yellow and green lines and a group of blue lines. The second spectrum of krypton is characterised by a considerable number of lines, chiefly in the blue. The first spectrum of xenon exhibits a group of blue lines less refrangible than the group in the first krypton spectrum. The second xenon spectrum is even more complex than the second krypton spectrum, and is characterised by certain bright green lines which determine the colour of the discharge. The wave-lengths of all the lines observed are given in the paper and compared, where possible, with the data of other observers (Runge, *Astrophys. Journ.*, 1899, 10, 73; Liveing and Dewar, *Abstr.*, 1901, ii, 213, 598).

J. C. P.

Ultra-violet Spectrum of Radium. SIR WILLIAM CROOKES (*Proc. Roy. Soc.*, 1903, 72, 295—304, 413).—An induction spark was passed between platinum poles partly immersed in a strong solution of pure radium nitrate, slightly acidified with nitric acid. The position of the various lines was determined by comparison with an iron spectrum. Tables are given showing the wave-lengths, not only of the lines detected by the author, but also of those ascribed to radium by earlier investigators. Many of the latter lines were probably due to something else than radium and are not found in the author's list.

J. C. P.

Further Observations on the Spectrum of the Spontaneous Luminous Radiation of Radium at Ordinary Temperatures. Sir WILLIAM and Lady HUGGINS (*Proc. Roy. Soc.*, 1903, 72, 409—413).—The glow spectrum of radium bromide is found to coincide with the band spectrum of nitrogen. It appears, therefore, that the radium stimulation is unable to elicit from either the radium or the bromine molecules their characteristic line spectra. J. C. P.

Absorption of Light by Aqueous Solutions of Copper and Nickel Salts. E. MÜLLER (*Ann. Physik*, 1903, [iv], 12, 767—786).—The absorption within the limits of the visible spectrum is the same for all the copper salts investigated so long as the solutions are dilute. In concentrated solutions of cupric bromide and chloride, there is a further absorption in the blue and the violet; in concentrated solutions of the nitrate and acetate, there is a further absorption in the red. The molecular extinction coefficient (Beer's law) approaches a limiting value with increasing dilution, and this value is the same for all copper salts, in agreement with the theories of Knoblauch and Ostwald.

Concentrated solutions of nickel salts have very different tints, but in dilute solutions there is uniformity as in the case of the copper salts.

The colour of those salt solutions for which Beer's law is fulfilled within the limits of the visible spectrum is independent of the temperature. The fact that Beer's law is not valid for other solutions is doubtless to be attributed to the dissociation. J. C. P.

Influence of Great Dilution on the Absorption Spectra of Highly Concentrated Solutions of the Nitrates and Chlorides of Didymium and Erbium. JOHN EDWARD PURVIS (*Proc. Camb. Phil. Soc.*, 1903, 12, 206—211).—The absorption bands of very concentrated solutions of didymium and erbium chlorides are not affected by dilution. Those of concentrated solutions of the nitrates become less diffuse on dilution. The absorption bands of concentrated and dilute solutions of didymium and erbium chlorides correspond very closely with those observed in dilute solutions of the nitrates.

J. C. P.

Colour-sensitive Silver Chloride. EMIL BAUR (*Zeit. physikal. Chem.*, 1903, 45, 613—626).—It is found that all photochlorides (that is, mixtures of silver chloride and subchloride in different proportions) reproduce the solar spectrum in its proper colours, and it is considered probable that the various coloured modifications of the subchloride behave as optical antipodes. Evidence is brought forward also to show that silver chloride and subchloride most probably form homogeneous mixtures. J. C. P.

Polarimetric Researches. II. Rotation Dispersion in Solutions. CHR. WINTHER (*Zeit. physikal. Chem.*, 1903, 45, 331—377. Compare Abstr., 1902, ii, 589).—In order to find how far the rational dispersion coefficient (*loc. cit.*) retains the same value for various solutions of an optically active substance, the author has extended his

investigations to solutions of ethyl tartrate in benzene and *isobutyl* alcohol, and of propyl tartrate in benzene, *isobutyl* alcohol, and ethylene bromide. It is found that the rational dispersion coefficient is the same for all substances in the tartaric acid group, whether they are in the pure state or in solution. Equations are given connecting the specific rotation and the temperature for various solutions, and it is seen that the maximum temperatures in these equations are in the main independent alike of the wavelength of the light and the concentration of the solutions. The mean values of these maximum temperatures for all the substances of the tartaric acid group lie between 137° and 149° . In the case of substances exhibiting anomalous dispersion, a given change of rotation always involves a corresponding regular change of dispersion, whether this change is brought about by an alteration of temperature or an alteration of concentration. It is further shown that the influence of the solvent on the dispersion is in the main constant and independent of the concentration. This fact finds expression in the calculation of a solution dispersion coefficient—a constant which varies with the nature of the solvent and the active solute. J. C. P.

Phenomena of Luminosity and their Possible Correlation with Radioactivity. HENRY E. ARMSTRONG and T. MARTIN LOWRY (*Proc. Roy. Soc.*, 1903, 72, 258—264).—One of the authors has previously pointed out (*Abstr.*, 1902, ii, 546) that luminous manifestations may be attributed to oscillatory changes in molecular structure. This argument is developed, and it is shown that the occurrence of triboluminescence runs more or less parallel with the existence of isodynamic forms. Menthyl phenylformylacetate, which exists in two such forms, not only is triboluminescent, but gives out brilliant flashes of light as it separates from solution. Crystals of saccharin, unless highly purified, give off flashes of light when crushed, and this substance may be conceived as existing in two isodynamic forms. In neither of the above cases could any effect on the electrometer be detected. Another fact of importance is that triboluminescence is observed in the case of π -bromonitrocamphor, camphoroxime, and α -bromocamphor, which can all exist in isodynamic forms, whilst it is not observed in similar cases where isodynamic forms are impossible, for example, α -chloro- α -bromocamphor.

The phenomena of fluorescence and phosphorescence are discussed also from the point of view of isodynamic change, and it is suggested that radioactivity may be regarded as an exaggerated form of fluorescence in which radiations generally capable of penetrating substances are absorbed and rendered obvious. Thorium and thorium X may be regarded as merely isodynamic forms of thorium, behaving very similarly to the isodynamic forms of nitrocamphor. It is pointed out that the properties referred to in this paper are common to many substances. Uranium nitrate is not only radioactive, but triboluminescent, fluorescent, and phosphorescent at low temperatures. Platinocyanides are triboluminescent, fluorescent, and phosphorescent at low temperatures. It is possible, therefore, that these several

luminous manifestations may have a common origin in isodynamic change. J. C. P.

Penetrating Radiation from the Earth's Surface. H. LESTER COOKE (*Phil. Mag.*, 1903, [vi], 6, 403—411).—With a gold leaf electroscope, it is shown that there ordinarily exists everywhere a radiation comparable as regards penetrating power with that from radium. This radiation accounts for 30—33 per cent. of the natural ionisation commonly observed in testing vessels, a conclusion deduced from the reduction of ionisation effected by using massive lead screens. The penetrating radiation may be due to the radioactive matter which is distributed throughout the earth and the atmosphere.

A number of materials, such as brick, dried earth, polished tin, writing paper, stone, pine-wood, lead, zinc, and iron were found on examination to emit a radiation of a not very penetrating character, a phenomenon which probably accounts for the residual ionisation in an electroscope surrounded by heavy metal screens; this activity was found to be less for brass than for any of the materials just mentioned.

With the author's arrangement of the testing apparatus, it is found that the number of ions produced per c.c. per second in air under atmospheric pressure is 5 (compare the number 14, found by C. T. R. Wilson). J. C. P.

The Scintillating Phosphorescence which Certain Substances present under the Action of the Radium Rays. HENRI BECQUEREL (*Compt. rend.*, 1903, 137, 629—634).—In view of the explanation of the scintillating phosphorescence of the spinthariscopes offered by Crookes (*Abstr.*, 1903, ii, 461), the author has completed a series of experiments started some years ago (*Abstr.*, 1900, ii, 126), with the object of ascertaining (1) whether a part only of the radium rays is concerned in the phenomenon, and (2) whether the scintillations are really due to the impact of the electrons on the screen, or if they are not rather to be attributed to a change in the molecular structure of the material composing the screen induced by the action of the exciting rays.

In order to investigate the first point, thin mica screens coated with various phosphorescent materials in a fine state of division were exposed to the rays emitted by a small quantity of radium chloride, and preliminary experiments, in which a thin sheet of aluminium was placed between the radium chloride and the screen, showed that the scintillating phosphorescence was excited by those rays which are most readily absorbed and consequently least penetrating.

In another series of experiments, the separate effects of the α - and β -rays on the screens were examined by placing the radium chloride in a lead block between the poles of an electromagnet, and the results obtained confirmed Crookes' opinion that the α -rays only induce the scintillating phosphorescence; the phosphorescence excited by the β -rays, if appreciable or preponderating, masks the phenomenon produced by the α -rays.

The question whether the scintillations are to be attributed to the

impact of the electrons on the screen or to the molecular disintegration of the material forming the screen is not so easily solved; but evidence in favour of the latter alternative is afforded by the fact that the state of aggregation of the material composing the screen plays a very important part in the phenomenon. When a relatively large crystalline fragment of hexagonal blende is exposed to radium rays, it becomes phosphorescent, but shows no scintillations; if the same crystal is broken into very small pieces, it exhibits under the same conditions variable brilliant points of light, whilst if it is pulverised the characteristic scintillations appear. A similar luminous effect is produced when the crystals are broken mechanically between plates of glass (compare Armstrong and Lowry, this vol., ii, 5). M. A. W.

Scintillation of Phosphorescent Zinc Sulphide in the presence of Radium, Revived by Electric Discharges. THOMAS TOMMASINA (*Compt. rend.*, 1903, 137, 745—747).—Screens of zinc sulphide which have been exposed to the action of radium rays and then kept in the dark for some time exhibit phosphorescence, but no scintillation. The phosphorescence of a screen which has been covered with a glass plate is distributed equally over the surface, whilst an unprotected screen exhibits several dark points and a single bright one. The scintillations on each screen can be revived, but to an unequal extent, by the action of positive or negative electric discharges, the unprotected screen still exhibiting the dark points, but the scintillations being as bright as those initially produced by the radium rays. The dark points correspond with cavities in the crystalline layer, and the scintillations are most vivid at the more prominent edges of the crystals. These facts point to an electrostatic origin of the light phenomenon, which consists in the irregular production of discharges resulting in the cleavage of the crystal (compare Becquerel, preceding abstract). M. A. W.

Heat given out by Radium. CARL RUNGE and J. PRECHT (*Sitzungsber. K. Akad. Wiss. Berlin*, 1903, 783—786).—To estimate the heat given out by radium, the authors have determined the current which must be supplied to a small platinum spiral so that the latter shall, under the same conditions, produce the same temperature difference as the radium salt. They find, in good agreement with Curie and Laborde (Abstr., 1903, ii, 346), that one gram of radium gives out 105 cal. per hour. From an experiment similar to the foregoing, in which the radium salt was enclosed in a leaden cell, the authors conclude that the kinetic energy of the particles shot off from radium constitutes only a small part (probably less than 5 per cent.) of the total heat developed. Hence, on the assumption that the particles shot off from radium move with not less than a tenth of the velocity of light, it is shown that one gram of radium would in 1000 years lose less than one-half of a milligram in weight.

If it is assumed that the heat given off from a radium salt is dependent only on the amount of radium it contains, a comparison of the amounts of heat evolved from equal quantities of the chloride and

bromide furnishes a method of calculating the atomic weight of radium. J. C. P.

Activity Induced by Thorium. F. VON LERCH (*Ann. Physik*, 1903, [iv], 12, 745—766).—The decline of the activity induced on metals by the emanation from thorium follows in all cases the same exponential law (compare Rutherford and Soddy, *Trans.*, 1902, 81, 841). If the metals are dissolved, the activity becomes associated with the ions, and if the metal is precipitated as an insoluble compound, the precipitate is active. If the induced activity on a piece of metal is dissolved by treatment for several minutes with hot dilute hydrochloric acid, and the active solution thus obtained is electrolysed between inactive platinum electrodes, the cathode becomes intensely active, the anode remains inactive. When amalgamated zinc is used as cathode, the same result is obtained, and the activity falls off in the same manner as the ordinary induced activity. The rate of decline of the activity is somewhat greater with a platinum cathode. It is possible to obtain the activity at the other electrode if silver is used as anode and the chlorine is fixed as silver chloride; if the active silver chloride thus obtained is reduced by zinc in presence of hydrochloric acid, part of the activity is transferred to the zinc.

The author's experiments favour the view that the solution of the activity from metal plates by hydrochloric acid is electrolytic in character. Copper, tin, lead, nickel, iron, cadmium, zinc, magnesium, and aluminium immersed in such an active solution, become active; platinum, palladium, and silver remain inactive. The activity thus deposited falls off at a rate which varies in different cases, and from this the author draws conclusions as to its composition. The chief portion, the decline of which corresponds with that of the ordinary induced activity, is assigned a place in the potential series between copper and lead, close to hydrogen.

The results obtained indicate generally that the activity induced by thorium is of a material character. J. C. P.

Change of Electrical Resistance of Selenium under the Influence of Certain Substances. ARTHUR B. GRIFFITHS (*Compt. rend.*, 1903, 137, 647).—When a piece of selenium was exposed at a distance of 5 cm. from an alcoholic solution of the pigment from geranium petals for about 15 minutes, its electrical resistance, determined by the Wheatstone bridge method, fell from 462,000 ohms to 320,000 ohms. Similar results were obtained with other vegetable and animal pigments. As van Aubel (*Abstr.*, 1903, ii, 403) has already shown that a reduction in the electrical resistance of selenium is effected by light, radium, and Röntgen rays, the author suggests that the pigments emit these rays. M. A. W.

Conditions determining the Sign and Magnitude of "Contact" Electrification. JEAN PERRIN (*Compt. rend.*, 1903, 137, 513—514).—The author has investigated the sign and magnitude of the electrification produced by contact of a solid with a liquid by observing the movement (*electric osmose*) induced in the same liquid by

an electric charge equal in amount and opposite in kind, and finds that the charge resulting from contact is generally greatest with liquids of high ionising capacity (such as water), and is due to the ions present in the liquid. In aqueous solutions, the ions $+H$ and $-HO$ alone are active, and each of these charges the diaphragm (that is, the immersed solid) with electricity of its own sign. This method of detecting free $+H$ and $-HO$ ions is more delicate than that of coloured indicators such as litmus.

The activities of $+H$ and $-HO$ ions are diminished by the presence respectively of negative and positive polyvalent ions, and the magnitude of this paralysing action increases with the concentration of the polyvalent ions.

In conformity with these views are the statements of (a) Picton and Linder, that colloids probably exist in aqueous solution in the form of electrically charged granules; (b) of Hardy, that the sign of this charge is extremely sensitive to the influence of traces of acids and alkalis, and (c) of Schulze and of Hardy, that the coagulation of colloids is brought about most readily by electrolytes capable of furnishing a polyvalent ion carrying a charge opposite in sign to that of the colloidal granules, and is the more effective the greater the charge of this ion (compare Abstr., 1903, ii, 469).

T. A. H.

Electromotive Forces resulting from the Contact and Reciprocal Action of Two Liquids. MARCELLIN P. E. BERTHELOT, (*Compt. rend.*, 1903, 137, 956—957. Compare Abstr., 1903, ii, 526, 626).—The author's former papers have shown the importance of utilising electrically the chemical energy developed by reactions between solutions.

C. H. D.

Reproduction of the Electromotive Forces of some Strong Oxidising Agents. J. SCOBAL (*Zeit. Elektrochem.*, 1903, 9, 879—887).—It has been frequently observed that the difference of potential between a platinum electrode and a solution of an oxidising agent is affected by the acidity of the latter, but the values of the potential differences are so variable and uncertain that no definite connection between them can be found.

The author has experimented with $1N$, $12N$, and $22N$, and anhydrous sulphuric acids saturated with manganese dioxide, potassium permanganate, chromium trioxide, and sodium persulphate, and with different varieties of platinum and iridium electrodes. He finds that, after a few days, the potential differences attain constant values, which are, as a rule, independent of the electrode used. With chromic acid, the potentials fall a little on shaking, but soon regain their original values. For the concentrated solutions used, it appears, therefore, that the potential differences measured are really constant and reproducible quantities.

T. E.

Electrical Conductivity of Flames. FERNAND VANDEN BOSSCHE (*Bull. Acad. Roy. Belg.*, 1903, 864—887. Compare Hemptinne, Abstr., 1902, ii, 119).—The author confirms the statement of Smithells, Dawson, and Wilson (Abstr., 1899, ii, 722), that the electrical con-

ductivity of a flame containing a vaporised metallic salt is not dependent on the dissociation of the salt by water vapour in the flame and subsequent ionisation of the metallic hydroxide produced, as was suggested by Arrhenius (Abstr., 1891, 515).

The author has investigated the phenomenon of unipolar conduction shown by flames containing vaporised salts, and finds that the extent to which this phenomenon is exhibited is dependent on the nature of the metal and appears to have some relationship to the valency of the latter, being most marked in the case of univalent metals such as sodium and potassium.

Unipolar conduction is also shown by a flame containing finely-divided metallic platinum, but not by flames containing bromine or chlorine. The unipolar conductivities of flames containing salts of univalent elements increases with the concentration of the salt solution injected, but this effect is less marked in the case of salts of bivalent metals. On the other hand, the effect of a change in the voltage of the current is much greater with flames containing salts of bivalent metals than with those containing salts of univalent elements.

The author points out that the statement of Wilson (Abstr., 1899, ii, 723), that unipolar conduction of flames containing vaporised salts is the result of the difference in the velocities of the positive and negative ions into which the salt is dissociated, leads to the conclusion that flames containing salts of barium and strontium should show more marked unipolar conduction than those containing potassium and sodium salts, which is in opposition to the experimental results now brought forward. He explains the differences exhibited in this respect by salts of univalent and bivalent metals by assuming that ionisation of the salts occurs only where the gas is in contact with the electrodes, and principally at the negative electrode, which, it is further assumed, exerts a greater ionising influence on salts of univalent elements than on those of bivalent elements, and that, consequently, there is a greater flow of electricity from the negative electrode in the former case. This would also explain the greater effect induced by change of voltage in the case of salts of the bivalent metals.

T. A. H.

Conductivity of Mixtures of Electrolytes. FERDINAND BARM-WATER (*Zeit. physikal. Chem.*, 1903, 45, 557—565. Compare Abstr., 1899, ii, 396).—The author deduces an expression for the conductivity of binary mixtures of organic acids, and the theoretical deductions are tested by experiments on mixtures of acetic acid with glycollic, propionic, butyric, or valeric acid; of propionic acid with butyric or valeric acid; and of butyric acid with valeric acid. The agreement is exceedingly good for mixtures of acetic and glycollic acids, and least satisfactory for mixtures of acetic and valeric acids.

J. C. P.

Can the Formation of Complexes be Deduced from the Electrolytic Conductivity of Mixtures of Acids? ROBERT HOFMANN (*Zeit. physikal. Chem.*, 1903, 45, 584—588).—The author shows that whilst the laws of isohydric solutions apply in the case of (1) hydrochloric and sulphuric acids, (2) chromic and sulphuric acids,

they do not apply in the case of chromic and hydrochloric acids, the conductivity of a mixed solution of the last two acids being markedly different from the calculated value. The conclusion to be drawn is that these two form complexes in solution, the existence of which tendency is already known. J. C. P.

History of the Electrolysis of Water. ALBERT NEUBURGER (*Ber.*, 1903, 36, 3572—3574).—The discovery that hydrogen and oxygen are the only products of the electrolysis of water and that the production of alkali at the cathode and acid at the anode is due to impurity in the water is usually credited to Davy, who commenced his experiments in 1800, but did not publish this result until 1806. This fact had been observed by P. L. Simon, and was published in *Gilbert's Annalen*, 1801, 8, 41 and 492; 9, 386, five years before Davy's communication appeared. T. M. L.

Complex Ions of Zinc and Cadmium. HANS EULER (*Ber.*, 1903, 36, 3400—3406. Compare *Abstr.*, 1903, ii, 544).—The solubility of zinc hydroxide in ammonia solutions of different concentration increases much more rapidly than the concentration of the ammonia.

It has not been found possible to calculate the dissociation constant K for the zinc-ammonia complex from the equation

$$K = 4D[\text{NH}_3]_4 / [\text{Zn}(\text{NH}_3)_4]_3,$$

where D denotes the ionisation product, $\text{Zn}^{++} \times (\text{OH})_2^-$.

The values for K calculated from the *E.M.F.* of concentration cells, metal | hydroxide in ammonia | 0.05*N* sulphate | metal, were as follows: for Zn, $K = 2.6 \times 10^{-10}$, and for Cd, $K = 1.0 \times 10^{-7}$. The zinc-ammonia complex, $\text{Zn}(\text{NH}_3)_4^{++}$, is thus some 100 times as stable as the cadmium-ammonia complex, $\text{Cd}(\text{NH}_3)_4^{++}$.

For the anions $\text{Zn}(\text{CN})_4^-$ and $\text{Cd}(\text{CN})_4^-$, the following values have been obtained for K , by a similar method, namely, 1.3×10^{-17} and 1.4×10^{-17} .

Abegg's theory of valency is adversely criticised.

J. J. S.

New Method for the Determination of Freezing Points of Fused Electrolytes. OTTO LIEBKNECHT and ERLING NILSEN (*Ber.*, 1903, 36, 3718—3721).—The freezing point of a fused electrolyte may be accurately determined by measurements of the electrical conductivity, by Kohlrausch's method, at short intervals (every 5° or 10° of temperature). The freezing point is indicated by a sudden change in the direction of the curve. Carbon electrodes give a sharper minimum than metal. The temperature is determined by a thermo-couple. For high conductivities, a three-limbed tube of hard glass is suitable, the electrodes being plunged into the outer limbs and the thermoelement in the centre limb. Curves are given for several mixtures of commercial salts. The freezing point of a mixture of potassium chloride and sodium fluoride is identical with that of a mixture of sodium chloride and potassium fluoride. C. H. D.

Heats of Combustion of Organic Compounds viewed as Additive Properties. Alcohols, Phenols, Ethers, Aldehydes, and Ketones. PAUL LEMOULT (*Compt. rend.*, 1903, 137, 515—517. Compare Abstr., 1903, ii, 410).—By assigning the values 51, 130, and 210 Cal. to the influences exerted respectively by single, double, and triple linkings of carbon to carbon, on the molecular heats of combustion of hydrocarbons, and of 53 Cal. to that due to carbon linked to hydrogen, the author has shown that the mol. heats of combustion of a number of hydrocarbons can be calculated (*loc. cit.*). This investigation has now been extended to the classes of oxygenated carbon compounds enumerated in the title by the use of further suitable conventional values.

For primary and secondary saturated alcohols, the influence of the group $\text{:C}\cdot\text{OH}$ = 8 Cal.; for phenols and saturated tertiary alcohols, this is diminished to 2 Cal., and for unsaturated alcohols it becomes -4 Cal. The influence of the group $\text{:C}\cdot\text{O}\cdot\text{C}$: in saturated ethers is estimated at 18 Cal., and for unsaturated ethers at 6 Cal. In saturated aldehydes, the effect of the carbonyl group is 12 Cal., and in saturated ketones, 6 Cal., these values being in each case diminished by 12 Cal. in the case of the unsaturated compounds.

The mol. heats of combustion of a number of compounds calculated in this way are given in the original, and shown to agree with those determined experimentally. T. A. H.

Calculation of the Heats of Combustion of Organic Acids, their Anhydrides and Esters. PAUL LEMOULT (*Compt. rend.*, 1903, 137, 656—658).—The author finds that the heats of combustion of saturated organic acids, their anhydrides and esters, like those of the hydrocarbons, alcohols, ethers, aldehydes, and ketones (Abstr., 1903, ii, 410; preceding abstract), is a linear function of the number of carbon atoms in the molecule, the relation being represented by the general equation $\gamma = 157x + A$, where γ is the heat of combustion, x the number of carbon atoms in the molecule, and A a constant the value of which depends on the nature of the compound. For monocarboxylic acids, $A = -106$; for dicarboxylic acids -212; and for esters -90. Similar conventions are given for the calculation of the heat of combustion of corresponding derivatives of the aromatic series and the unsaturated aliphatic series. M. A. W.

A New Method for the Calculation of Heats of Combustion and some of its Consequences. PAUL LEMOULT (*Compt. rend.*, 1903, 137, 979—982. Compare Abstr., 1903, ii, 410).—The molecular heat of combustion of any hydrocarbon C_xH_y containing only single linkings is given by $(102x + 27\cdot5y)$ Cal., trimethylene being an exception. For hydrocarbons containing one double linking, this is increased by 28 Cal., and for one triple linking by 57 Cal. Compounds containing oxygen have their heat of combustion diminished by a quantity ϕ , which has a separate value for each function, the value for a compound $\text{C}_x\text{H}_y\text{O}_p$ becoming $(102x + 27\cdot5y - \Sigma p\phi + K)$ Cal. The values of ϕ and K are tabulated for a number

of different classes of compounds. The value of K for a quadruple linking, such as would exist in a molecule C_2 , may be obtained by extrapolation.
C. H. D.

The Temperature of Flames. CHARLES FÉRY (*Compt. rend.*, 1903, 137, 909—912).—The author has devised a method of measuring the temperature of flames which does not involve the introduction of a solid body into the flame, but depends on the principle that when the light rays emitted by a luminous body pass through a monochromatic flame, the bright lines characteristic of the spectrum of the latter disappear (are reversed) when the temperature of the luminous body becomes the same as that of the flame. The luminous body employed was the filament of an incandescent lamp, and the temperature was determined by means of the absorption pyrometer used in the determination of the temperature of the electric arc (*Compt. rend.*, 1902, 134, 1201); the flames under investigation were rendered monochromatic by means of sodium or lithium salts, and the following results were obtained:

| | | |
|--|----------------|---|
| Bunsen burner | Air holes open | 1871° (mean of 8 determinations, limits 1855° and 1895°) |
| | „ „ half open | 1812 |
| | „ „ closed | 1712 |
| Acetylene flame | | 2548 |
| Alcohol, free flame | | 1705 |
| Vapour of alcohol burning in a Bunsen burner..... | | 1862 |
| Same lamp (alcohol mixed with 50 per cent. of benzene)..... | | 2053 |
| Hydrogen burning freely in air..... | | 1900 |
| Blow-pipe (coal gas and oxygen).... | | 2200 |
| „ (hydrogen and oxygen)... | | 2420 |

M. A. W.

Measurement of the Pressure Coefficient of Oxygen at Constant Volume and Different Initial Pressures. WALTER MAKOWER and HENRY R. NOBLE (*Proc. Roy. Soc.*, 1903, 72, 379—385).—The authors have determined, with the apparatus previously used by Travers and Jaquerod (*Abstr.*, 1903, ii, 9), the coefficient of increase of pressure for oxygen between 0° and 100°, the initial pressures being 375 and 700 mm. The value of the coefficient found increases slightly with the initial pressure, and on linear extrapolation to zero initial pressure lies between 0·003664 and 0·003665.

The thermodynamical correction at 0° is calculated for oxygen, and with this correction the authors find $\theta_0 = 273\cdot09$, where θ_0 is zero temperature on the thermodynamic scale. This value is in good agreement with that found by Callendar for air, nitrogen, and hydrogen (see *Phil. Mag.*, 1903, [vi], 5, 48).
J. C. P.

Vapour Pressures of Liquid Oxygen on the Scale of the Constant Volume Oxygen Thermometer filled at different Initial Pressures. MORRIS W. TRAVERS and CHARLES J. FOX (*Proc. Roy. Soc.*, 1903, 72, 386—391. Compare Travers, Senter, and Jaquerod, *Abstr.*, 1903, ii, 9).—Using the apparatus previously

described (*loc. cit.*) and taking the value of the pressure coefficient of oxygen found by Makower and Noble (preceding abstract), the authors show that the temperatures on the oxygen scale at which liquid oxygen has certain vapour pressures are lower than the corresponding temperatures on the helium scale. The deviation varies with the initial pressure in the oxygen thermometer, and is found on linear extrapolation of the observed values to be 1.5° at 1000 mm. initial pressure and 0.4° at zero initial pressure. J. C. P.

Determination of Vapour Densities at High Temperatures. FRIEDRICH EMICH (*Monatsh.*, 1903, 24, 747—764).—The author describes the application of Bunsen's method to the determination of vapour densities at temperatures between 1400 — 1900° . The apparatus consists of a cylindrical vessel, maintained at a constant temperature by a water jacket, from which the gas is driven over into a heated tube, terminating in the small opening through which the gas escapes. The opening, the shape of which is of some importance, may be in the centre of the tube. The temperatures of the vessel and of the tube must be kept constant, but the latter need not be known, in which case the apparatus is standardised with a gas known not to dissociate at the temperature of experiment. As the mercury rises in the vessel, it closes two electrical circuits, which, in conjunction with a second pendulum, gives the rate of flow of the gas. More constant results are obtained with porcelain than with platinum or iridium tubes. G. Y.

The Elasmometer, a New Interferential Form of Elasticity Apparatus. ALFRED E. H. TUTTON (*Phil. Trans.*, 1903, A, 202, 143—163).—An improved apparatus for determining the coefficient of elasticity of crystals. J. C. P.

Diffusion and Supersaturation in Gelatin. HARRY W. MORSE and GEORGE W. PIERCE (*Zeit. physikal. Chem.*, 1903, 45, 589—607).—It has been shown by Liesegang that when the end of a capillary tube containing a gelatin solution of potassium chromate is dipped in a solution of silver nitrate, the silver chromate precipitated by the diffusion of the silver nitrate is not equally distributed, but is concentrated in laminæ at right angles to the axis of the tube. Ostwald considers this to be a supersaturation phenomenon, and supposes that precipitation occurs when the limit between the metastable and labile conditions has been crossed. The authors have now made a theoretical and quantitative experimental study of the precipitation of silver chromate under the above-mentioned conditions, and found the numerical value of H , the constant metastable concentration product—a quantity analogous to the solubility product for two ions in presence of the solid electrolyte. H is defined by the equation $[Ag^+]^2[CrO_4^{''}] = H$, and determines the limit of supersaturation for silver chromate when the solid phase is absent. The value found for H is 1.4×10^{-6} , and this means that the concentration of silver chromate in the gelatin when precipitation begins is 145 times as great as that required for saturation in presence of the solid.

In the course of their work, the authors have shown that the distance between the laminæ of silver chromate in any given tube, at a given temperature, and for given concentrations of the reacting substances is governed by the relationship $x/\sqrt{t} = \text{const.}$, where x is the distance from the end of the tube of a lamina formed t seconds from the time of dipping in the silver nitrate. The time of formation of a lamina could be exactly determined, for it took place suddenly.

The value found for the diffusion constant of silver nitrate in gelatin containing silver chromate is 1.54.

Liesegang observed a similar formation of laminæ in the cases of mercurous chromate, lead chromate, and Prussian blue, and the authors have obtained the same result with lead sulphate, silver carbonate, phosphate, bromide and thiocyanate, cobalt hydroxide, barium chromate, and mercurous bromide. J. C. P.

Course of the Solubility Curve in the Region of Critical Temperatures of Binary Mixtures. ANDREAS SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 171—181).—The course of a solubility curve of a solid in the region of critical temperatures is discussed. Experiments were made with ether and anthraquinone, which were introduced into a tube at -80° and then sealed up. The temperature was then observed at which all the anthraquinone dissolved. When the mixture consists of 45 per cent. of ether and 55 per cent. of anthraquinone, below 195° there is excess of solid anthraquinone together with a saturated solution and vapour. At about 195° , the first critical temperature is reached, when, if more heat be added, the solution disappears and the phases consist of solid anthraquinone and vapour. At 241° , the liquid phase is regenerated, and, on further rise of temperature, more anthraquinone gradually dissolves, until at 247° it has all dissolved. With further increase of temperature, the region of unsaturated solution is reached, until at 350° the unsaturated solution has reached its critical temperature, and all passes into the gaseous state.

It was also shown with ether and anthraquinone that points in the metastable part of the critical curve could be determined. Vapours can be supersaturated towards the solid phase, and for their transition into the stable phase pass through the metastable phase, namely, a supersaturated solution.

The results of Walden and Centnerszwer (*Abstr.*, 1903, ii, 284) on the solubility of potassium iodide in liquid sulphur dioxide are discussed. A. McK.

Solubility of Ammonia in Salt Solutions, as Measured by its Partial Pressure. II. HANS RIESENFELD (*Zeit. physikal. Chem.*, 1903, 45, 461—464. Compare *Abstr.*, 1902, ii, 309).—A number of determinations, carried out as described in the earlier paper, have been made at 35° . The values thus obtained for the lowering of the solubility have been compared with the values previously obtained at 25° and with the values determined at 60° by Konowaloff. The only solutions for which a marked temperature coefficient exists are those of sodium and potassium carbonates, sodium and lithium chlorides.

In these cases, presumably, there is interaction between the ammonia and the dissolved salt. For sodium hydroxide, potassium hydroxide, chloride, nitrate, acetate and oxalate, the temperature coefficient is practically zero. It appears from the above that where there is interaction between ammonia and the dissolved salt, it is greater for sodium than for potassium salts, and greater for lithium than for sodium salts.

J. C. P.

Condition of Sodium Sulphate in Solution. CHARLES MARIE and R. MARQUIS (*Zeit. physikal. Chem.*, 1903, 45, 566—570).—According to Wyruboff (Abstr., 1901, ii, 149), a solution of sodium sulphate prepared from the hydrated salt contains hydrated molecules, and is not the same as one prepared from the anhydrous salt. If this were so, the solubility of sodium chloride in a solution of hydrated sodium sulphate should exhibit a sudden increase at the temperature of transition of the decahydrate. The authors, whose experiments have been made at temperatures between 14.8° and 34.3° , find no trace of any such discontinuity (compare also Hantzsch, Abstr., 1903, ii, 145).

J. C. P.

Velocity of Decomposition of Ammonium Nitrite. II. KURT ARNDT (*Zeit. physikal. Chem.*, 1903, 45, 571—583. Compare Abstr., 1902, ii, 64).—A consideration of detailed points raised by Blanchard's paper (Abstr., 1903, ii, 18). In particular, the author argues against Blanchard's view that the velocity of decomposition increases with the concentration of the NO_2' ions, for it can be shown that the presence of potassium nitrite has no effect. The accelerating effect of other nitrites, such as those of sodium and barium, is probably due to their hydrolytic dissociation and the consequent formation of nitrous acid (compare Arndt, *loc. cit.*). The author estimates that in 0.3*N* solution, sodium nitrite is hydrolytically dissociated to the extent of 0.1 per cent., barium nitrite to the extent of 0.32 per cent.

The affinity constant of nitrous acid has been determined, and the value found to be very slightly different from that obtained by Schumann (see Blanchard, *loc. cit.*).

J. C. P.

The Laws of Displacement of Chemical Equilibrium. E. ARIÈS (*Compt. rend.*, 1903, 137, 738—741. Compare Abstr., 1903, ii, 589). From purely mathematical considerations, the author deduces the relation $dvdp - dsdT < 0$, where dv and ds denote respectively the variation of volume and entropy due to chemical action in a system. By making $dT = 0$ or $dp = 0$, the relation becomes the mathematical expression of the two laws of the displacement of chemical equilibrium due to Le Chatelier and van't Hoff, namely, (i) at constant temperature, the chemical change produced by an increase of pressure involves a contraction of volume. (ii) At constant pressure, the chemical change produced by increase of temperature is endothermic.

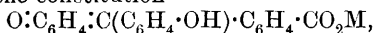
M. A. W.

Exceptions to the Phase Rule, especially in the Case of Optically Active Substances. ALFRED BYK (*Zeit. physikal. Chem.*, 1903, 45, 465—495).—In his lecture on the phase rule, van't Hoff pointed out that it was possible to construct out of the two components,

H_2O and NaClO_3 , a system containing five phases, namely, vapour, solution, inactive salt, and the two active forms, that is, one more than the phase rule allows. Van't Hoff concluded that the phase rule should be supplemented by the introduction of molecular conceptions, and Wegscheider (*Abstr.*, 1903, ii, 356) adopted a similar view of the insufficiency of the phase rule. In the present theoretical paper, which is in general unsuitable for abstraction, the author shows that thermodynamical treatment gives a perfectly adequate interpretation of the observed phenomena, even in the case of optically active substances. It is only necessary to modify somewhat the definition of a 'phase' commonly given in thermodynamical text-books. J. C. P.

Conception of Independent Components. II. RUDOLF WEGSCHEIDER (*Zeit. physikal. Chem.*, 1903, 45, 496—504).—A reply to van Laar's criticisms (*Abstr.*, 1903, ii, 536). J. C. P.

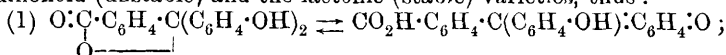
Theories of Indicators. JULIUS STIEGLITZ (*J. Amer. Chem. Soc.*, 1903, 25, 1112—1127).—The "chromophoric" theory of indicators is preferred by the author to the "ionisation" theory. The explanation, for instance, that phenolphthalein should become intensely red by forming an ion without a chromophoric group appeared, from the outset, as extremely unlikely. It is more probable that phenolphthalein in its colourless solution has the constitution of a lactone, whilst its salts are derivatives of a carboxylic acid and not of a phenol and have the constitution



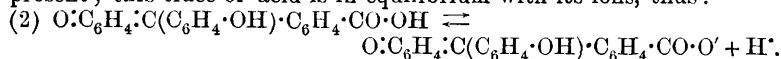
with the strongly chromophoric quinonoid complex $\text{:C}_6\text{H}_4\cdot\text{O}$. The sodium salt is incidentally ionised; this ionisation is a coincidence and not a cause, since the solid, dry, non-ionised silver salt is also intensely coloured.

Methyl-orange is taken as a type of an amphoteric indicator. In alkaline solution, it is probable that metallic salts of methyl-orange, $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, containing the azo-grouping, are produced, whilst in acid solution red salts of methyl-orange, $\text{SO}_3\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}:\text{C}_6\text{H}_4\cdot\text{NMe}_2$, of the quinonoid constitution, are formed. [Compare also Vaillant, this vol., i, 119.]

In an aqueous solution of phenolphthalein, it is supposed by the author that a condition of equilibrium is established between the quinonoid (unstable) and the lactonic (stable) varieties, thus:



the condition of equilibrium favours the lactonic form, since the solution is colourless and only traces of the quinonoid acid can be present; this trace of acid is in equilibrium with its ions, thus:



The addition of alkali causes the disappearance of the hydrogen ions, when more of the quinonoid molecules must be ionised in order that the equilibrium may be preserved; the quinonoid form must in turn be reproduced from the lactonic according to equation (1). The effect

of alkali, therefore, is to suppress the colourless lactonic isomeride by converting the unstable free quinonoid acid into its stable quinonoid salt, which is coloured red and is incidentally ionised.

The author adduces experimental evidence on the part of Hantzsch and others in support of his views.

The sensitiveness of indicators is also discussed.

A. McK.

Theory of Colloids and Suspensions. JEAN BILLITZER (*Zeit. physikal. Chem.*, 1903, 45, 307—330).—The author discusses the theories brought forward by Hardy and by Bredig, and finds them inadequate. According to Hardy, the addition of an electrolyte to a colloidal solution diminishes the potential difference between the colloid particles and the surrounding liquid, the point at which the potential difference vanishes being termed the “isoelectric” point. But it is pointed out that colloidal platinum, which under ordinary conditions travels towards the anode, can be made to travel in the opposite direction by the addition of alcohol, which, however, precipitates the colloid only very slowly. On the other hand, the addition of potassium chloride, which does not diminish the potential difference between the colloid and the liquid, precipitates the platinum in a few minutes. The author himself avoids the electrical double layer theory, and conceives the colloidal solution as containing charged particles of the colloid, which may be positive or negative, and may be outside the immediate sphere of action of the oppositely charged particles of the water. When an electrolyte is added, the charged particles of the colloid collect round the positive or negative ion as a nucleus, and, when heavy enough, the accumulated matter is precipitated. In support of this view, the author refers to the observation (compare Linder and Picton, *Trans.*, 1895, 67, 63; Spring, *Arch. Sci. phys. nat.*, [iv], 10, 305; Whitney and Ober, *Abstr.*, 1902, ii, 65) that the ion effective in the precipitation is oppositely charged to the colloid. Further, it is shown by experiments with the chlorides of barium, strontium, calcium, and potassium that the quantities of these various metals carried down by the precipitated colloid are in the ratio of their chemical equivalents. If potassium chloride is used as the precipitating electrolyte, acid is set free when the colloidal substance is electronegative, whilst alkali is liberated when the colloidal substance is electropositive.

Emphasis is laid on the complete analogy between regular colloidal substances and mechanical suspensions.

J. C. P.

Classification of Colloids. ARTHUR MÜLLER (*Zeit. anorg. Chem.*, 1903, 36, 340—345).—The author submits the following classification of colloids: (1) suspensions of fine particles, (a) where the medium is water or a liquid of less viscosity, (b) where the medium is a liquid of higher viscosity, for instance, colloidal silver chloride in gelatin solution (de Bruyn). (2) Solutions of compounds with high molecular weights.

A. McK.

Absorption Compounds of Hydrogel. JACOBUS M. VAN BEMMELEN (*Zeit. anorg. Chem.*, 1903, 36, 380—402. Compare *Abstr.*, 1902, ii, 70).—The criteria of “absorption compounds” are as follows. The

quantities absorbed are related in no equivalent proportion to the absorbing quantities; the composition depends on the structure of the absorbing substance and varies with the temperature. The composition also varies with the concentration of the surrounding vapour phase. The rate of formation of an absorption compound decreases as the absorption increases.

By dialysis of ferric chloride and sodium silicate respectively, the hydrosols of ferric oxide and silicon dioxide were prepared. The observations of Kohlrausch on the conductivity of sodium silicate solutions are interpreted on the supposition that sodium hydroxide and silicon dioxide hydrosol are gradually formed on the gradual dilution of a concentrated sodium silicate solution.

A small quantity of baryta suffices to convert ferric oxide sol into the hydrogel; baryta is absorbed by the latter, and equilibrium is established after some time. The quantities of baryta absorbed varied with different hydrosol preparations; the absorption is at first rapid. Barium chloride is also absorbed by the hydrogel.

From the ferric oxide hydrosol, strong acids separate a hydrogel, which, however, gradually dissolves.

Experiments with silicon dioxide hydrosol and baryta are also quoted. A small quantity of baryta converts the hydrosol into the hydrogel, by which baryta is also absorbed. When molecular proportions of silicon dioxide and barium hydroxide are taken, the crystalline barium silicate, $\text{BaSiO}_3 \cdot 6\text{H}_2\text{O}$, separates. Crystallographic measurements of the latter are quoted.

A. McK.

Colloidal Metals. JEAN BILLITZER (*Chem. Centr.*, 1903, ii, 982; from *Verh. Vers. Deutsch. Naturf. Aerzte*, 1902, 19—21. Compare *Abstr.*, 1902, ii, 454).—The addition of a certain amount of alcohol to an aqueous solution of colloidal platinum does not cause the colloid to move either to the anode or cathode, hence no potential difference is established. On the other hand, less colloid is precipitated by the alcohol than by an indifferent electrolyte. In the solution of an electrolyte, the positively charged colloidal or suspended particles attract the anions and condense on their surfaces, whilst the negatively charged particles behave in a similar manner towards the cations. Marble suspended in a solution of barium chloride, for instance, becomes positively charged and attracts the negative ion, thus leaving the solution alkaline, whilst powdered porcelain, under similar conditions, is negatively electrified and adheres to the positive ion, thus rendering the solution acid. Aggregation of the small particles in colloidal solutions in non-conducting liquids involves loss of free energy, but the consequent decrease of electrical capacity tends to raise the potential and to increase the free energy, hence the process of cohesion cannot take place spontaneously. Since the colloidal particles in solutions of electrolytes are rendered electrically neutral by the action of the ions, there is no increase of potential. In the case of suspended particles, the force of gravitation also comes into play.

E. W. W.

Fifth Report of the Atomic Weight Commission. HANS LANDOLT and WILHELM OSTWALD (*Ber.*, 1903, 36, 3759—3766).—A reply to Winkler (*Chem. Zeit.*, 1903, 76, 918), who urges the readoption of $H=1$ as the standard of atomic weights and protests against the insertion of $H=1.01$ in the international table of atomic weights in place of $H=1.0076$, the value given by E. W. Morley in 1890; the latter alteration corresponds with an alteration of Ag 107.93 to 108.18. In reply, it is pointed out that if $H=1$ be adopted as the standard, an alteration in the ratio $H:O$ from 15.88 to 15.87 would introduce a change in the atomic weights of other elements, which in the case of chlorine is four times, in the case of iodine eleven times, and in the case of mercury fifteen times as great as the probable error in the determination of the ratio $Cl:O$, $I:O$ and $Hg:O$; on the other hand, with $O=16$, the change in the atomic weight of hydrogen would only be from 1.0076 to 1.0082. It is further pointed out that the use of $H=1.01$ in place of 1.008 introduces an error of less than 0.02 in the percentage composition of the majority of hydrogen compounds.

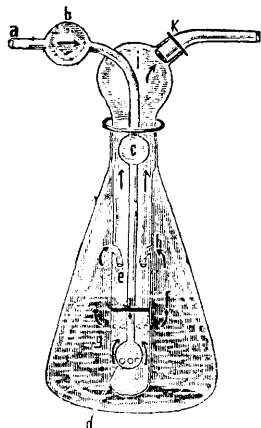
T. M. L.

Production of High Vacua for Chemical Distillation. ERNST ERDMANN (*Ber.*, 1903, 36, 3456—3461).—High vacua can readily be produced by filling a distilling apparatus with carbon dioxide under reduced pressure and cooling a part of the apparatus with liquid air. If rubber stoppers are eliminated, the vacuum of the cathode light can be produced; an apparatus with rubber connections gave a minimum pressure of 0.026 mm. Liquid carbon dioxide cannot be used, as it contains 0.75 vol. per cent. of air dissolved in it; the proportion of oxygen in this absorbed air is 24.1 per cent. Carbon dioxide snow gave good results, but the simplest arrangement is to prepare the gas from marble and hydrochloric acid, and, before condensing with liquid air, to exhaust to 30 mm. with a water pump; the apparatus is filled with carbon dioxide and exhausted three times in order to free it from air; merely passing the gas through the apparatus is not sufficient to displace the air in a reasonable time. The following examples are given: *o*-nitrobenzoyl chloride, b. p. 105° under 0.5 mm. pressure, m. p. of distillate, 20° ; glycerol, b. p. $115-116^{\circ}$ under 0.056 mm. pressure; 1:2-naphthylene diamine, b. p. $150-151^{\circ}$ under 0.48 mm. pressure; *p*-aminodiphenylamine, b. p. 155° under 0.026 mm. pressure.

T. M. L.

Triple Acting Wash and Absorption Bottle. C. GLATZEL (*Chem. Zeit.*, 1903, 27, 1060—1061).—The apparatus consists of the inlet tube, *a*, with two bulbs, *b* and *c*, to prevent the regurgitation of the liquid, and a third bulb, *d*, the lower portion of which is provided with very small openings. The inlet tube is sealed into a cylinder, *e*, which is ground air-tight into the bottle, and at *f* passes through a partition. At *g*, the cylinder contains a ring of small holes, and at *h* two tubes have been sealed. The bulb, *i*, is used for the reception of dry absorbers, which are introduced by means of the tube, *k*. The bottle is filled up to the mark with the absorbing liquid, and, as will be seen from the

figure, this stands, of course, higher in the narrow inlet tube, *a*, than in the wider cylinder, *e*. When gases are passed through, the liquid is expelled from the inlet tube and is forced into the surrounding cylinder, so that the small openings at *d* are always immersed in the liquid, even when there is a great pressure. The gas comes in a finely-divided state in contact with the liquid, is washed or absorbed, escapes through the openings, *g*, of the cylinder, and then passes again in a finely divided state through the liquid surrounding the cylinder into the empty space of the bottle. Thence it passes through the tubes *h* into the upper part of the ground cylinder, the bulb of which is filled with a dry absorber. Instead of this, a second liquid may also be used, which is poured through the tube *k* into the separate compartment of the cylinder to such a height that the tubes *h* are immersed.

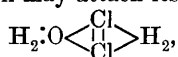


L. DE K.

Inorganic Chemistry.

Combination of Hydrogen and Chlorine under the Influence of Light. P. V. BEVAN (*Phil. Trans.*, 1903, *A*, 202, 71—121).—In addition to the work already described (see Abstr., 1902, ii, 237), the author has made a number of experiments bearing on the induction period. It is found that the induction period may be prolonged indefinitely, although its general character remains the same. If the chlorine has been illuminated before it is mixed with the hydrogen, the subsequent action of light on the mixture is more rapid to begin with, in other words, the induction period is shortened. This effect of previous illumination of the chlorine is destroyed by bubbling the chlorine through water. Previous illumination of the hydrogen has no effect on the period of induction. With Wilson's expansion method (*Proc. Camb. Phil. Soc.*, 9, 333), it has been shown that the formation of hydrogen chloride is preceded by the production of an intermediate substance, which can act as a condensation nucleus. The removal of this substance by expansion and consequent precipitation stops the production of hydrogen chloride, and the induction period has to begin over again. The observation that the combination of hydrogen and chlorine is much accelerated by the presence of water vapour, together with experiments just described, lead the author to assume the intermediate formation of a compound of chlorine and water, perhaps $\text{H}_2\text{:O} \begin{array}{c} \text{Cl} \\ \diagup \diagdown \\ \text{Cl} \end{array}$.

To this, a molecule of hydrogen may attach itself, forming



which finally breaks down into $\text{H}_2\text{O} + 2\text{HCl}$. This view, which in its general lines may be extended to other chemical reactions where the presence of water is necessary, explains the phenomena of the induction period and the effect of pre-insolation of the chlorine, and interprets also the observation that small quantities of impurities very markedly diminish the rate of action. In all gaseous reactions which are conditioned by the presence of a catalyst, a period of induction must be expected to occur, and the application of the mass action law to these cases must be made with reference to the intermediate compounds formed. It is not to be expected, therefore, that the law of mass action as applied to the end product equation will interpret the actual experimental results (compare, on this whole subject, Mellor, *Trans.*, 1901, 79, 216; 1902, 81, 1280, 1292). J. C. P.

Electrolytic Formation of Perchlorate. WILHELM OECHSLI (*Zeit. Elektrochem.*, 1903, 9, 807—828).—The oxidation of a chlorate to a perchlorate differs from the oxidation of an iodate to a periodate in the circumstance that the former is accompanied by a loss of free energy, whilst the latter is not. When the oxidation is carried out electrolytically, there are corresponding differences, the best yield of perchlorate being obtained with high current density at smooth platinum anodes, at low temperatures, and in neutral or acid solutions, whereas the yield of periodate is best at low current densities, and is little affected by temperature or by the acidity or alkalinity of the solution. The last-named characteristics are found in most cases of simple oxidation. The facts just mentioned, which the author has confirmed by means of a large number of electrolyses of solutions of chlorates, are best explained by the hypothesis that the formation of perchlorate is not due to a simple oxidation but takes place as follows: the ClO_3 group liberated primarily at the anode reacts with water giving oxygen and chloric acid. The highly concentrated solution of chloric acid so formed then decomposes spontaneously into perchloric and chlorous acids, the latter being then oxidised by the anodic oxygen to chloric acid. The process may be represented by the equations $2\text{ClO}_3' + \text{H}_2\text{O} + 2F = \text{HClO}_4 + \text{HClO}_2 + \text{O}$, and $\text{HClO}_2 + \text{O} = \text{HClO}_3$. The latter reaction is shown to take place by electrolysing solutions of chlorine dioxide and of alkali chlorites. Ozone is liberated at the anode when perchlorate is being produced, but the author finds by direct experiment that ozone is incapable of oxidising a solution of a chlorate; the formation of ozone has, therefore, nothing to do with the formation of perchlorate. T. E.

New Method for the Preparation of Pure Iodine. LAUNCELOT W. ANDREWS (*Amer. Chem. J.*, 1903, 30, 428—430).—The following method is described for the preparation of pure iodine from impure potassium iodide. The potassium iodide is powdered with 1.4 times its weight of potassium dichromate, each salt having been previously fused to ensure perfect dryness. The mixture is introduced into a wide tube

and heated at 200° in a current of dry air to expel the last traces of moisture. A plug of dry glass wool is placed over the mixture, which is then heated with a small flame. The iodine having been sublimed into the upper part of the tube, the latter, when cold, is cut off at a point 2—3 cm. above the glass wool plug. E. G.

Preparation of Pure Iodine. HENRI BAUBIGNY and PAUL RIVALS (*Compt. rend.*, 1903, 137, 927—929).—See this vol., ii, 81.

Derivation of Organic Polyvalent Iodine Compounds from Existing or Hypothetical Inorganic Iodine Compounds. CONRAD WILLGERODT (*Chem. Zeit.*, 1903, 27, 1132—1134. Compare *Abstr.*, 1903, i, 745, 746).—This paper contains an enumeration of various organic compounds, which may be regarded as derivatives of iodine trichloride, iodine trifluoride, the hypothetical iodine, IH_3 , the hypothetical hydroxyiodine, $\text{IH}_2\cdot\text{OH}$, the hypothetical acid, $\text{O}:\text{I}\cdot\text{OH}$, di-iodine, $\text{H}_2\text{I}\cdot\text{IH}_2$, iodine pentafluoride, iodine oxyfluoride, IOF_3 , iodic acid, the hypothetical periodic acid, $\text{IO}_3\cdot\text{OH}$, trihydroxy-periodic acid, $\text{IO}_2(\text{OH})_3$, chloric acid, bromic acid, and perchloric acid. A. McK.

Atomic Weight of Fluorine. JULIUS MEYER (*Zeit. anorg. Chem.*, 1903, 36, 313—324).—The results obtained by Davy, Berzelius, Louyet, Dumas, de Luca, Fremy, Moissan, and Christensen for the atomic weight of fluorine show considerable discrepancies. The author has accordingly studied the interaction of calcium oxide and hydrofluoric acid.

Ammonium carbonate, carefully purified by sublimation, was added to an aqueous solution of calcium nitrate and the precipitated calcium carbonate converted into oxide by heating it in a platinum crucible by means of an electric oven (compare Hinrichsen, *Abstr.*, 1902, ii, 137, 501). The calcium oxide was converted into calcium hydroxide, which was next converted into calcium chloride; by repeated evaporation of this with hydrofluoric acid, the fluoride was finally obtained. As a mean of five determinations, the value found was 19.036, with a probable error of ± 0.00149 ($\text{Ca} = 40.136$), a number slightly less than Moissan's. A. McK.

The Extraction of Oxygen by the Partial Liquefaction of Air with Reflux Action. GEORGES CLAUDE (*Compt. rend.*, 1903, 137, 783—786).—When air cooled to -160° is allowed to rise under a pressure of two atmospheres through vertical metal tubes kept in a bath of liquid air, it is partially liquefied, the liquid being slightly richer in oxygen than the ordinary air (compare *Compt. rend.*, 1903, 136, 1659—1662), is therefore in equilibrium with a gaseous phase less rich in oxygen than itself; the liquid falls in the tube and meets a gaseous phase of different composition, and equilibrium is restored by an exchange of nitrogen on the part of the liquid phase for oxygen from the gaseous phase; this process is repeated throughout the downward passage of the liquefied air until the final product may contain as much as 50 per cent. of oxygen.

By diminishing the pressure of the gas undergoing liquefaction, the condensation is less rapid, and the resulting liquid becomes richer in oxygen and the residual gas richer in nitrogen; thus, under a pressure of 0.7 atmosphere, one-third only of the air was liquefied, the final liquid phase contained 70 per cent. of oxygen, and the final gaseous phase 97—98 per cent. of nitrogen. An apparatus on a large scale, arranged by the Soc. de l'*Air liquide*, supplies 30—40 cubic metres per hour of liquid air containing 92 per cent. of oxygen. M. A. W.

Ozone. LEOPOLD GRÄFENBERG (*Zeit. anorg. Chem.*, 1903, 36, 355—379. Compare Abstr., 1902, ii, 449).—The amount of ozone in the oxygen evolved in the electrolysis of hydrofluoric acid increases with the current density, but is not proportional to it. At the temperature of the laboratory, the yield of ozone did not exceed 5.2 per cent. of the amount theoretically obtainable from the direct action of fluorine on water. The anodes were destroyed during the electrolysis.

The oxidation potential of ozone was determined. The *E.M.F.* of 10 per cent. ozone in potassium hydroxide gave 1.65 volt.

A new theory for the formation of ozone is formulated.

The existence of ozonic acid, H_2O_4 , is regarded as possible.

A. McK.

Influence of the Electrolyte and the Electrodes on Ozone Formation. ROBERT KREMANN (*Zeit. anorg. Chem.*, 1903, 36, 403—411. Compare Luther and Inglis, Abstr., 1903, ii, 406; Gräfenberg, preceding abstract).—With 2 volts, the author was unable to detect ozone in the electrolysis of sulphuric, chromic, and phosphoric acids. With equal potential and equal current density, the yield of ozone was greater in those cases where the surface of the anode was small. Experiments were made with sulphuric, phosphoric, and chromic acids, where the anodes consisted of platinum, nickel, gold, and lead peroxide.

In sulphuric acid solution, the formation of ozone proceeds more readily with lead peroxide than with platinum. When the concentration of the acid is about 4 mols. per litre, the yield of ozone reaches its optimum. With increase of surface of the anode, the influence of concentration of the various acids used disappears. All the electrodes employed appear to decompose the ozone formed. Sulphuric acid was the most favourable electrolyte with the various electrodes; lead peroxide is best for phosphoric acid and platinum for chromic acid solutions. Ozone is formed from potassium hydroxide at low temperatures only.

A. McK.

Ozonising of Oxygen by the Silent Electric Discharge. E. WARBURG (*Sitzungsber. K. Akad. Wiss. Berlin*, 1903, 1011—1015. Compare following abstract).—The silent electric discharge took place from a metallic point kept at a constant measured potential between 4000 and 12,000 volts, and the amount of ozone produced was compared with the quantity of electricity passing through the gas. The ozone produced was always under 1 per cent. of the maximum amount that could be obtained in the apparatus.

When the potential is negative, the quantity of ozone per coulomb is for a given current independent (1) of the potential difference of the electrodes, and (2) of the character of the earthed electrode. The quantity of ozone per coulomb decreases slowly as the current increases. When the potential is positive, the quantity of ozone per coulomb increases rapidly with the current; for small currents, its value is less than with negative potential, for larger currents it is greater. The work expended in the production of 1 gram of ozone by the above method is calculated for the most favourable case, and found to be about 34 times as great as the equivalent of the heat absorbed in the formation of 1 gram of ozone. For the production of 1 gram equivalent of ozone, not more than 500 coulombs are required, and it is therefore improbable that the process involved in the production of ozone by the silent electric discharge is at all similar to electrolysis. The author considers that the production of ozone by the silent electric discharge may be attributed to photo- and cathodo-chemical action.

J. C. P.

Production of Ozone by the Silent Electric Discharge in Siemens' Ozone Apparatus. ARTHUR W. GRAY (*Sitzungsber. K. Akad. Wiss. Berlin*, 1903, 1016—1020. Compare preceding abstract).—The quantity of ozone per coulomb produced in the author's apparatus is 0.27 gram, a value 4—5.5 times greater than that obtained by Warburg, using a point discharge. The ozone per coulomb is independent of the potential difference between the electrodes of the generator, and probably also of the quantity of electricity used.

J. C. P.

Temperature of Ignition and Slow Combustion of Sulphur in Oxygen and in Air. HENRI MOISSAN (*Compt. rend.*, 1903, 137, 547—553).—The method employed for carbon (*Abstr.*, 1903, ii, 141) gave results for the ignition point of octahedral sulphur varying between 275° and 280°; it was modified by maintaining the sulphur in an atmosphere of carbon dioxide and heating the oxygen by allowing it to bubble through the fused sulphur. Below 282°, sulphur dioxide was formed without any incandescence; when this temperature was reached, the reaction became more vigorous, a slight explosion occurred, followed immediately by incandescence. The ignition point of sulphur in air was found to be 363°; this is raised by the presence of 5 per cent. of sulphur dioxide to 445°, and when 10 per cent. is present, ignition does not occur at 465°. The point of ignition of sulphur vapour in air is much lower than that of liquid sulphur, being about 285° (compare, however, *Hill, Abstr.*, 1890, ii, 849).

The slow combustion of sulphur in oxygen in sealed tubes, at temperatures below 150°, was studied by cooling the gaseous products in liquid air; it was found that, even at 20°, after the lapse of a month, the production of sulphur dioxide could be detected in this way.

Similar results were obtained with prismatic and amorphous sulphur; the action is much slower in air, but traces of sulphur dioxide could be detected at the end of three months when the temperature was maintained at 16—26°.

M. A. W.

Radioactivity and Atomic Weight of Tellurium. GIOVANNI PELLINI (*Gazzetta*, 1903, 33, ii, 35—42).—The author suggests that the explanation of the fact that tellurium gives a higher atomic weight than iodine, and so makes these elements occupy abnormal positions in the periodic system of the elements, is due to the presence in the tellurium of a small quantity of an element which has a higher atomic weight (about 212), is similar to tellurium, and analogous to the radioactive constituents of pitch-blende (compare Marckwald, *Abstr.*, 1903, ii, 81).
T. H. P.

Dimorphism of Telluric Acid. B. GOSSNER (*Zeit. Kryst. Min.*, 1903, 38, 499—501).—Telluric acid, $\text{Te}(\text{OH})_6$, crystallises in two modifications, a cubic (sp. gr. 3.053) and a monoclinic (sp. gr. 3.071); detailed crystallographic descriptions are given of each. The latter, although pseudo-rhombohedral in habit, is not hexagonal as previously described (*Abstr.*, 1896, ii, 97; 1901, ii, 649).
L. J. S.

Orthonitric Acid. HUGO ERDMANN (*Zeit. angew. Chem.*, 1903, 16, 1001—1004).—The author has submitted experimental evidence for the existence of orthonitric acid, $\text{N}(\text{OH})_5$ (*Abstr.*, 1903, ii, 73). Küster (*ibid.*, 939) denies the existence of this compound on what the author considers as very scanty experimental evidence. Küster further claims to have isolated the hydrates $\text{HNO}_3 \cdot \text{H}_2\text{O}$ and $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$. These substances were discovered not by Kuster but by Pickering (*Trans.*, 1893, 63, 436).
A. McK.

Hydrates of Nitric Acid. FRIEDRICH W. KÜSTER (*Zeit. angew. Chem.*, 1903, 16, 1079—1080).—Polemical. A reply to Erdmann (compare preceding abstract).
A. McK.

Metaphosphates. FRIEDRICH WARSCHAUER (*Zeit. anorg. Chem.*, 1903, 36, 137—200).—An historical review of the chemistry of metaphosphates is first given.

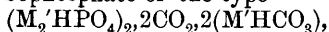
Copper metaphosphate, $(\text{CuP}_2\text{O}_6)_n$, prepared by adding copper oxide to an excess of about 5 per cent. of crystallised phosphoric acid at a temperature not exceeding about 448° , is indefinite as to crystalline form. It is decomposed with difficulty by hydrogen sulphide, and, when the resulting solution is neutralised by sodium hydroxide, sodium metaphosphate, $(\text{Na}_2\text{P}_2\text{O}_6)_n \cdot 2n\text{H}_2\text{O}$, is formed. Barium metaphosphate was prepared from barium carbonate and phosphoric acid. Aluminium metaphosphate crystallises from water in tetrahedra. Lead metaphosphate is prepared from phosphoric acid and lead oxide at a temperature not exceeding 400° . Determinations of electrical conductivity and transport numbers, made with the sodium salt, prepared by the double decomposition of copper metaphosphate and sodium sulphide, indicated that this sodium salt has the composition $\text{Na}_4\text{P}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$. Potassium metaphosphate loses its water of crystallisation at 100° ; determinations of its electrical conductivity pointed to its having the composition $\text{K}_4\text{P}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$. The ammonium salt of the composition $(\text{NH}_4)_4\text{P}_4\text{O}_{12}$ (deduced from the conductivity deter-

minations quoted) is anhydrous; its crystals, which are tetragonal, were measured. The lithium salt, $\text{Li}_4\text{P}_4\text{O}_{12}\cdot 4\text{H}_2\text{O}$, is sparingly soluble in water, and in this respect differs from lithium ortho- and pyrophosphates. The silver salt is anhydrous.

When the lead salt, prepared at a temperature below 400° , interacts with sodium sulphide, the resulting sodium salt is identical with the salt prepared from copper metaphosphate and sodium sulphide. A different lead salt is formed when the temperature of formation exceeds 400° , and, when this substance is decomposed by sodium sulphide, it forms a sodium salt, which, from the conductivity measurements quoted, appears to be sodium hexametaphosphate.

A quantitative separation of pyrophosphate from metaphosphate cannot be accomplished by Fremy's luteocobaltichloride. A. McK.

Action of Carbon Dioxide under pressure on the Metallic Phosphates. A. BARILLÉ (*Compt. rend.*, 1903, 137, 566—568).—The author finds that the metallic phosphates may be divided into two classes with respect to their behaviour towards carbon dioxide under pressure in the presence of water: (1) those which, like calcium phosphate (Abstr., 1902, ii, 258), combine with the carbon dioxide to form a soluble carbophosphate, and (2) those which simply dissolve in the carbonic acid without undergoing any decomposition. The metals, the phosphates of which belong to the first class, are those of the alkalis and the alkaline earths (sodium, potassium, ammonium, calcium, barium, and magnesium), which are capable of forming hydrogen carbonates; the normal phosphates of these metals appear to form a [tribasic] carbophosphate of the type



which decomposes in the presence of air forming the monohydrogen phosphate and hydrogen carbonate of the metal; whilst the monohydrogen phosphates give a [dibasic] carbophosphate of the type $(\text{M}_2'\text{HPO}_4)_2, 2\text{CO}_2$, which, on decomposition, regenerates the original salt.

M. A. W.

Sublimed Carbon. MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1903, 137, 589—594).—The author has examined the sublimate of carbon formed on the inner surfaces of incandescent lamps, using a current of 70—80 volts; under these conditions, the temperature of the carbon filament probably ranges from 1200 — 1500° . The sublimate dissolved entirely when treated with nitric acid and potassium chlorate, and therefore consisted solely of amorphous carbon. Similar experiments made (a) with raw, hydrogen-free carbon filaments, and (b) with "used" carbon filaments, from both of which mineral matter had been previously removed by treatment with ammonium fluoride and sulphuric acid, indicated that these also consisted of amorphous carbon. The formation of a sublimate in incandescent lamps under these conditions indicates that carbon exerts an appreciable vapour tension at temperatures about 2000° below its boiling point (3600°). This unusually large interval is regarded as further evidence of the highly complex character of the molecules of solid carbon.

T. A. H.

A Filamentous Variety of Carbon. CONSTANT and HENRI PELABON (*Compt. rend.*, 1903, 137, 706—708).—A form of carbon wool is sometimes met with in the upper portions of recuperative coke-ovens, especially at the aperture for the exit of the hot gases. The wool consists chiefly of grey cylindrical threads with glazed surface, sometimes showing a series of expansions, and occasionally bearing bundles of much finer black threads. The average length of the threads is 5 cm., even attaining 8 cm., the diameter varies from 0.03 to 0.15 mm., the black threads being perhaps only 0.002 mm. When heated in dry oxygen, combustion only begins at 585° and is complete, only 0.4 per cent. of ash being found. A mixture of nitric acid and potassium chlorate oxidises the carbon to graphitic acid.

The formation of filamentous carbon is probably due to the decomposition of heavy hydrocarbon vapours by heat. C. H. D.

Artificial Diamonds. RUDOLF VON HASSLINGER and JOSEF WOLF (*Monatsh.*, 1903, 24, 633—647. Compare Abstr., 1903, ii, 142).—The authors have investigated the effect of variations in the composition of the fusion mixture, and of variations in the rate of cooling after fusion, on the formation of artificial diamonds.

Experiments in which the period of cooling after fusion varied from 10 minutes to 50 hours showed this factor to be without influence on the formation of diamonds or on the size of diamonds formed.

Diamonds are formed in such fusion mixtures only as have a crystalline structure when cooled. The presence of alkalis, calcium and magnesium oxides, and between 45 and 60 per cent. of silica is necessary. A mixture containing a larger proportion of silica does not yield diamonds. The silica may be replaced by titanium dioxide but not by boric acid.

The authors consider that the carbon forms a carbide with a metallic element in the fusion mixture, decomposition of the carbide with liberation of the carbon in the crystalline form follows under favourable conditions.

Diamonds were obtained from a mixture to which carbon had been added only in the form of calcium carbide. G. Y.

[Decomposition of Carbon Monoxide.] Correction. RUDOLF SCHENCK (*Ber.*, 1903, 36, 3663—3664. Compare Abstr., 1903, ii, 423).—A few corrections of the numbers contained in the previous paper. These do not, however, affect the main deductions already given. J. J. S.

Argon in the Atmosphere. HENRI MOISSAN (*Compt. rend.*, 1903, 137, 600—606).—The author has repeated the determinations made by Schloesing (Abstr., 1896, ii, 166, 219) and by Kellas (Abstr., 1896, ii, 661) using, however, as a principal absorbent of oxygen and nitrogen a red-hot mixture of lime and magnesium (Maquenne, Abstr., 1896, ii, 299), and, as a final absorbent, red-hot metallic calcium, which also removes any traces of hydrogen (Abstr., 1899, ii, 25, 155). A large

number of samples of air from different parts of the globe, including specimens collected at London, Berlin, and Paris, the summit of Mont Blanc, and on the Atlantic Ocean, were examined. The amounts of argon found in samples of air collected on land at altitudes varying from 0 to 5800 mètres were, as a rule, between 0.932 and 0.935 per cent., and agree with those found by Schlösing and by Kellas. In the case of those specimens collected over open seas, slightly higher amounts were obtained, reaching 0.9492 per cent. in the case of one specimen collected over the Atlantic Ocean in Lat. 43 N. and Long. 22, 10' W.

T. A. H.

New Preparation of Argon. HENRI MOISSAN and ALBERT RIGAULT (*Compt. rend.*, 1903, 137, 773—777).—The authors have obtained pure argon from the atmosphere at the rate of 1 litre in 12 hours by taking advantage of the property calcium possesses of forming a crystalline nitride, Ca_3N_2 , and hydride, CaH_2 , stable at 500°. Atmospheric nitrogen was passed through tubes containing powdered magnesium and quick lime (3:5) at a red heat; this increased the quantity of argon to 10 per cent.; a similar operation under diminished pressure was repeated until the final product contained only 5—10 per cent. of nitrogen; this was removed, together with traces of hydrogen, by passing the gas through a tube heated to dull redness and containing crystalline calcium in nickel boats.

M. A. W.

Radioactive Gas in Surface Water. H. A. BUMSTEAD and L. P. WHEELER (*Amer. J. Sci.*, 1903, [iv], 16, 323).—A radioactive gas was obtained from a spring near New Milford, Conn., at a depth of 1500 feet. The water from one of the New Haven city reservoirs (an artificial lake fed entirely by surface drainage) also contained a gas which was strongly radioactive. The gas drawn from the ground, at a depth of about 5 feet, proved to be about three times as radioactive as the gas from the surface water.

A. McK.

Electrolysis of Alkali Chlorides. II. Production of Sodium Hydroxide in Diaphragm Electrolysis. PHILLIPE A. GUYE (*Arch. Sci. phys. nat.*, 1903, [iv], 16, 393—416).—Two methods of procedure are in use in diaphragm electrolysis: (1) the electrolysis is carried on until the cathode liquid has a given alkalinity, when it is entirely withdrawn and replaced by a fresh solution; (2) the cathode solution is maintained at approximately a constant strength, being fed continuously by a salt solution. The first method is that which gives the best yield for the same electrical energy, and the two cases are considered and expressions deduced for concentration after the passage of a definite quantity of electricity. In the second type of electrolysis, two cases are considered: (1) when the feeding solution does not mix with the remainder, (2) when complete mixture is instantaneous. In the first of these, the current yield is equal to that obtained in the previous type of electrolysis. Neither of these cases actually occurs in practice, but the first case approximates to that obtaining when the cathode compartment is large and the current density small; the

second is more nearly realised when the cathode compartment is small and the current density is high (compare Abstr., 1903, ii, 586).

L. M. J.

Purification of Brine by Barium Carbonate. GEORGES ARTH and P. FERRY (*Bull. Soc. chim.*, 1903, [iii], 29, 1065—1068).—It has been stated by Kosmann that the sulphates of calcium and magnesium frequently present in natural brines may be eliminated by digestion of the brine with the calculated quantity of barium carbonate, the sulphuric acid being precipitated as barium sulphate and the calcium as carbonate, whilst the magnesium remains in solution. The authors find that the elimination of calcium by this process is fairly complete, but that the sulphuric acid is only completely precipitated by digestion of the brine with three times the calculated quantity of barium carbonate for 3 hours at 100°. Numerical data and curves are given in the original showing the rate of elimination of the acid by digestion of the brine with various proportions of barium carbonate at 10° and 100°, and the amounts of barium carbonate dissolved by brine and also by solutions of (a) magnesium chloride and (b) of sodium chloride.

T. A. H.

Examination of some Artificially Prepared Compounds. P. VON SUSTSCHINSKY (*Zeit. Kryst. Min.*, 1903, 38, 264—272).—Crystallographic descriptions are given of the following:

Regular octahedral crystals of the alloys NaCd_2 and Mg_2Sn , prepared by N. S. Kurnakoff (Abstr., 1900, ii, 277).

Titanite prepared by E. van der Bellen in the manufacture of crystalline glazes on porcelain. Chalk, quartz, and rutile in the proportions required for titanite ($\text{CaO}, \text{TiO}_2, \text{SiO}_2$) were fused at a temperature of over 1400°. Cavities in the crystalline mass of titanite contained honey-yellow, acicular crystals.

"Copper-glance" from smelting works in the Altai. Bluish-black cubic (not orthorhombic) crystals of cuprous sulphide; they contain 8.93 per cent. of iron, but this may be present as an impurity.

L. J. S.

Relation of Rubidium to Potassium and Cæsium as Illustrated by the Crystalline Forms of Uranyl Double Salts. A. SACHS (*Zeit. Kryst. Min.*, 1903, 38, 496—498).—Potassium uranyl nitrate, $(\text{UO}_2)(\text{NO}_3)_2 \cdot \text{KNO}_3$, is orthorhombic, whilst the corresponding rubidium and cæsium salts are rhombohedral and isomorphous. This indicates that a closer relation exists between rubidium and cæsium than between rubidium and potassium. A review of the chemical and crystallographic literature bearing on this point is given.

L. J. S.

Acid Reaction of Ammonium Salts towards Blue Litmus. C. REICHARD (*Chem. Zeit.*, 1903, 27, 1105—1106).—Blue litmus paper, when immersed in aqueous solutions of ammonium chloride varying from 1 to 10 per cent., did not turn red, but when subsequently exposed to the atmosphere reddening took place. A similar observation was made with solutions of ammonium bromide and ammonium oxalate respectively.

A. McK.

Polymorphism of Nitrates. FRÉD. WALLERANT (*Compt. rend.*, 1903, 137, 805—807).—In addition to the four systems in which ammonium nitrate is known to crystallise, the author finds a fifth and probably a sixth by cooling the monoclinic form to the temperature of solid carbon dioxide; under these conditions, the crystals break down into hemitropic plates which slowly change into homogeneous uniaxial crystals belonging to the rhombohedral system. Cæsium nitrate, which crystallises in the cubic system just below its melting point and becomes rhombohedral on cooling, changes into the cubic system when cooled in liquid air, but the crystals are not isomorphous with the original. M. A. W.

Colours of Allotropic Silver. J. C. BLAKE (*Amer. J. Sci.*, 1903, [iv], 16, 282—288).—The white, blue, and red forms of silver appear to be sufficiently distinct to be regarded as allotropic forms. Yellow silver is possibly a variety of red silver. The colours in transmitted light are most marked with the colloidal solutions of the various forms of silver, whilst the colours in reflected light can be best noted with the silver mirrors. A table is given, where the appearance of the silver, reduced by different agents from aqueous solution of silver nitrate ammoniacal solution of silver nitrate, ammoniacal solution of silver oxide, suspension of silver oxide in water (filtered after treatment), and aqueous solution of silver nitrate (slightly acidified with sulphuric or nitric acids) respectively, is described. A. McK.

Colloidal Silver. ALFRED LOTTERMOSER (*J. pr. Chem.*, 1903, [ii], 68, 357—368).—A reply to Hanriot (*Abstr.*, 1903, ii, 597). In preparations of colloidal silver, other colloids are present as impurities and are not essential. Lea's soluble silver contains only traces of impurities. G. Y.

Colloidal Silver Haloids. ALFRED LOTTERMOSER (*J. pr. Chem.*, 1903, [ii], 68, 341—343. Compare *Abstr.*, 1898, ii, 116, 514).—Colloidal silver iodide is formed by addition of silver nitrate solution to potassium iodide solution, with or without the presence of ammonia, if the solutions are not stronger than 2 per cent., and the potassium iodide is kept in slight excess. With concentrated solutions or in the presence of ammonium chloride (compare Denigès, *Abstr.*, 1896, ii, 387), the silver iodide is precipitated in the "molecular" state. Colloidal silver iodide is difficult to purify from ammonia by dialysis.

When a solution of silver iodide in potassium iodide is poured into a large excess of water, colloidal silver iodide is not formed, but finely-divided, crystalline silver iodide is precipitated.

Colloidal silver bromide, but not the chloride, is formed under the same conditions as the iodide, but in absence of ammonia. G. Y.

Action of Metals and other Substances on Silver Bromide. RICCARDO BETTINI (*Nuovo Cimento*, 1903, [v], 5, 349).—The oxidising action exerted by oxidisable metallic laminæ on silver bromide photographic plates has been attributed to the vapours of the metal evolved in

very small quantity from the metallic surface. The author shows, however, that such metals, on oxidation, evolve hydrogen peroxide and ozone, which are capable of producing fog or images on bromide plates.

T. H. P.

Formation of Complexes. RICHARD ABEGG (*Ber.*, 1903, 36, 3684—3687).—A reply to Euler's criticisms (*Abstr.*, 1903, ii, 717) on the author's rule with regard to electro-affinities and the formation of complexes.

J. J. S.

Spontaneous Decomposition of Silver Peroxynitrate. EDUARD MULDER (*Rec. trav. chim.*, 1903, 22, 385—386. Compare *Abstr.*, 1896, ii, 561; 1897, ii, 260, 551; 1899, ii, 483, and 1900, ii, 724).—On November 28, 1895, the author set aside a specimen of silver peroxynitrate, $3\text{Ag}_2\text{O}_2\cdot\text{AgNO}_3\cdot\text{O}_2$, and has since then determined annually its loss of weight (due to evolution of oxygen) during the period ending December 18, 1901. From the tables given in the original, it appears that the average weekly loss of oxygen per gram of the salt varied from 0.000038 gram in the sixth year to 0.000067 in the fourth year. The loss of oxygen is stated to take place from that part of the molecule represented by $\text{AgNO}_3\cdot\text{O}_2$.

T. A. H.

Electrolysis of an Aqueous Solution of Silver Selenate. EDUARD MULDER (*Rec. trav. chim.*, 1903, 22, 387).—An electric current was passed for 72 hours through a saturated solution (0.835 gram per litre) of silver selenate in water without effecting any change. This negative result, taken in conjunction with the fact that selenic acid acts as an oxidising agent towards hydrochloric acid, indicates, in the author's opinion, that an acid of the formula H_2SeO_5 cannot exist.

T. A. H.

Action of Hydrogen Peroxide on Silver Oxide, Peroxide, Carbonate, and Nitrate. EDUARD MULDER (*Rec. trav. chim.*, 1903, 22, 388—400. Compare von Baeyer and Villiger, *Abstr.*, 1901, ii, 315, 654; Berthelot, *ibid.*, 383).—Weighed quantities of the silver compounds were treated with an aqueous solution of hydrogen peroxide, and at the end of the reaction the whole was evaporated to dryness at the atmospheric temperature in a desiccator under reduced pressure and the changes in weight, if any, determined. The results indicated that silver oxide, peroxide, and nitrate were recovered almost quantitatively from this treatment, but that silver carbonate was partially converted into the oxide. The hydrogen peroxide was decomposed in contact with the oxide, peroxide, or carbonate of silver, but not with the nitrate. There was also a slight evolution of oxygen and a small loss of weight when silver peroxynitrate was treated with hydrogen peroxide. The following equations are suggested as explaining typically the catalytic decomposition of hydrogen peroxide by silver compounds: $2(\text{HO}\cdot\text{OH}) + \text{Ag}_2\text{O} = 2(\text{HO}\cdot\text{OAg}) + \text{H}_2\text{O}$
 $2(\text{HO}\cdot\text{OAg}) = \text{Ag}_2\text{O} + \text{H}_2\text{O} + \text{O}_2$.

T. A. H.

New Reaction of Silver Peroxide. EDUARD MULDER (*Rec. trav. chim.*, 1903, 22, 401—404).—Silver peroxide dissolved in sulphuric acid gives a blue coloration with diphenylamine dissolved in the same liquid. The blue coloration produced by the addition of hydrogen peroxide to a solution of diphenylamine in sulphuric acid attains its maximum intensity, in ordinary circumstances, in two hours, then becomes green and finally brown. This brown substance is insoluble in water but dissolves in sulphuric acid giving a bluish-green colour. The blue colour is more stable in the absence of air, and its change to green may be temporarily inhibited by the addition of more sulphuric acid at the point when maximum intensity is reached. If fuming sulphuric acid be employed as a solvent for one or both of the reacting substance, a more permanent violet or bluish-violet coloration is produced. T. A. H.

Structural Formula of the so-called Silver Peroxynitrate. EDUARD MULDER (*Rec. trav. chim.*, 1903, 22, 405—406. Compare Abstr., 1896, ii, 561; 1897, ii, 260, and preceding abstracts; Sulc, Abstr., 1897, ii, 99, and Tanatar, Abstr., 1902, ii, 73).—The author states that although no compound of fluorine and oxygen has been isolated it is not impossible that Tanatar's compound, $2\text{Ag}_3\text{O}_4\cdot\text{AgF}$, may really have the structure $3\text{Ag}_2\text{O}_2\cdot\text{AgFO}_2$, analogous to that suggested by the author for silver peroxynitrate, $3\text{Ag}_2\text{O}_2\cdot\text{AgNO}_5$, the unstable group, AgFO_2 , being maintained in equilibrium by the residue of the molecule. Tanatar's formulæ for these compounds are objectionable since they imply the existence of silver oxides of the formulæ Ag_3O_4 and AgO_2 , which are, so far, unknown. T. A. H.

Remarkable Case of Spontaneous Crystallisation of Gypsum. STANISLAS MEUNIER (*Compt. rend.*, 1903, 137, 942—944).—Balls of plaster of Paris, after immersion for a short time in sea water, were allowed to dry; under these conditions some of the specimens assumed a crystalline structure, for on breaking them open, the interior, beyond a compact crust of about 4 or 5 mm. thickness, was found to be full of crystals 5 mm. long; in some cases, fissures appeared on the surface of the balls and they opened spontaneously, showing that the crystallisation is accompanied by a contraction of volume.

The author attributes the phenomenon to the power sea salt possesses of inducing crystallisation, and suggests that the natural crystalline deposits of gypsum may be due to the same cause.

M. A. W.

The First Anhydrous Modification of Calcium Sulphate. PAUL ROHLAND (*Zeit. anorg. Chem.*, 1903, 36, 332—339. Compare Abstr., 1902, ii, 601; 1903, ii, 545).—The substance (anhydrite 1) formed by heating gypsum above 130° is distinct from the hemihydrate and from Estrich gypsum (anhydrite 2) and, although it can be hydrated, is unsuitable for moulding purposes. The influence of various catalysts on the hydration of these different varieties of calcium sulphate has been studied by the author. Potassium

dichromate, the sulphates of potassium, sodium, and aluminium, the nitrates of sodium and potassium accelerate the hydration of anhydrite, and the hemihydrate, whilst ammonium chloride and magnesium chloride retard the hydration. Sodium chloride accelerates the hydration of anhydrite 2 and the hemihydrate, but is indifferent in the case of anhydrite 1. Anhydrite 1 appears to be a transitional compound between anhydrite 2 and the hemihydrate.

Three theories are advanced in connection with the behaviour of anhydrite 1. The acceleration of the rate of hydration may be due to the ease with which the resulting compound crystallises; anhydrite 1 does not set, because no nucleus of gypsum is present; formation of complex ions may be assumed, anhydrite 2 setting in presence of positive catalysts (for instance, sodium sulphate) only.

Anhydrite 1 is more stable than anhydrite 2, since the former requires a longer time to set than the latter. A. McK.

Solubility of Calcium Sulphate in Aqueous Solutions of Sulphuric Acid. FRANK K. CAMERON and J. F. BRFAZEALE (*J. Physical Chem.*, 1903, 7, 571—577. Compare Abstr., 1902, ii, 75, 207).—The temperatures at which determinations have been made are 25°, 35°, and 43°, and within this range there is no indication of the maximum solubility found for calcium sulphate in pure water (compare Hulett and Allen, Abstr., 1902, ii, 656). If the solubility of calcium sulphate in sulphuric acid is expressed by plotting the weight of calcium sulphate per litre against the weight of sulphuric acid per litre, a curve is obtained which rises to a maximum and then falls off. The positions of the maximum points are as follows: at 25°, 75 grams of H_2SO_4 and 2.84 grams of CaSO_4 per litre; at 35°, 85 grams of H_2SO_4 and 3.70 grams of CaSO_4 per litre; at 43°, 105 grams of H_2SO_4 and 4.26 grams of CaSO_4 per litre. A saturated solution of calcium sulphate in pure water is found to contain 2.126 grams of CaSO_4 per litre at 25°, and 2.145 grams of CaSO_4 per litre at 43°. For the initial increase of solubility in presence of sulphuric acid, a phenomenon which is apparently opposed to the hypothesis of electrolytic dissociation, explanations are suggested, but not tested.

The introduction of sulphuric acid and calcium sulphate into water is found to cause a contraction or condensation of the solvent.

J. C. P.

Formation of Oceanic Salt Deposits. XXXIII. Deposition of the Calcium Salts Anhydrite, Glauberite, Syngenite, and Polyhalite at 25°. JACOBUS H. VAN'T HOFF and F. FARUP (*Sitzungsber. K. Akad. Wiss. Berlin*, 1903, 1000—1010. Compare van't Hoff and Chiaraviglio, Abstr., 1900, ii, 284; Basch, Abstr., 1901, ii, 168; van't Hoff and Wilson, *ibid.*, ii, 249; van't Hoff, *ibid.*, ii, 558).—The results of a number of previous investigations are discussed and summarised, the conditions of formation of the various substances in presence of each other being represented in the usual graphical manner. It appears that in the evaporation of sea water at 25°

the calcium separates first of all as anhydrite, then as polyhalite, and finally again as anhydrite. J. C. P.

Gypsum and Anhydrite. JACOBUS H. VAN'T HOFF, E. FRANKLAND ARMSTRONG, WILLY HINRICHSSEN, FRITZ WEIGERT, and G. JUST (*Zeit. physikal. Chem.*, 1903, 45, 257—306. Compare Abstr., 1902, ii, 74; 1903, ii, 368).—The present paper, in the main a summary and review of work previously described (*loc. cit.*), contains some new matter.

The vapour tension of gypsum in forming natural anhydrite is greater than that observed in forming soluble anhydrite, and the corresponding relation between tension and temperature is given by the equation $\log p = \log p' + 1.486 - 500/T$. This leads to the value 63.5° as the temperature of transition of gypsum into natural anhydrite. In presence of sodium chloride or bromate, the transition takes place at a lower temperature, and from experiments with these salts another formula was deduced, leading to the value 66° for the transition temperature; the former value, however, is considered more trustworthy.

From the various equations giving the relation of tension and temperature, the following heats of hydration q (that is, for 1 kilogram-molecule of water) have been calculated: (1) gypsum from hemihydrate, $q = 2614$ Cal; (2) gypsum from soluble anhydrite, $q = 2370$ Cal; (3) gypsum from natural anhydrite, $q = 2303$ Cal; (4) hemihydrate from soluble anhydrite, $q = 1638$ Cal; (5) hemihydrate from natural anhydrite, $q = 1370$ Cal. Further, the heat of transformation (per kilogram-molecule) of soluble into natural anhydrite is 134 Cal.

The knowledge gained of the relative stability of the various forms of calcium sulphate leads to a survey of their solubilities. If the heat of precipitation of gypsum, which is positive below, and negative above, 37° , is assumed to diminish in a linear manner with the temperature, the solubility of gypsum is given by the formula $\log c = 46.8675 - 16.25(134.7/T + \log T)$, and the values calculated by this formula agree closely with those determined by Hulett (Abstr., 1901, ii, 493; 1903, ii, 260). Similarly, the solubility of anhydrite above 63.5° is given by the formula $\log c = 45.3815 - 16.25(103.9/T + \log T)$. For the solutions saturated with the metastable hemihydrate, the following applies: $\log c = 45.7475 - 16.25(108.5/T + \log T)$.

If E is the work done when a kilogram-molecule of water is taken up by calcium sulphate, $E = 2 T \cdot \log p'/p$, where p' and p are the vapour tensions of water and hydrate respectively at the temperature T . If this relationship is combined with the tension-temperature equations, the following values of E are obtained: (1) gypsum from hemihydrate, $E = 737 - 6.88t$; (2) gypsum from soluble anhydrite, $E = 602 - 6.48t$; (3) gypsum from ordinary anhydrite, $E = 435 - 6.84t$; (4) hemihydrate from soluble anhydrite, $E = 197 - 5.28t$; (5) hemihydrate from ordinary anhydrite, $E = -471 - 6.72t$. In these various equations, the conditions of equilibrium find their simplest expression, the transition temperatures being those values of t obtained when E is zero. J. C. P.

Solubility of Magnesium Carbonate in Aqueous Solutions of Certain Electrolytes. FRANK K. CAMERON and ATHERTON SEIDELL (*J. Physical Chem.*, 1903, 7, 578—590. Compare Abstr., 1902, ii, 320).—The solubility of magnesium carbonate in sodium chloride solutions of increasing concentration rises to a maximum and then falls off. With an atmosphere containing only carbon dioxide and water vapour at atmospheric pressure, the solubility of magnesium carbonate (as magnesium hydrogen carbonate) in sodium chloride solutions diminishes regularly as the sodium chloride concentration increases. The solubility of magnesium carbonate in sodium sulphate solutions, under the same conditions, increases slightly and then decreases with rising sodium sulphate concentration. With an atmosphere free from carbon dioxide, the solubility of magnesium carbonate increases and then decreases in solutions of sodium chloride, whilst in solutions of either sodium sulphate or carbonate it regularly increases with the concentration. The solubility of magnesium carbonate in sodium sulphate solutions, in the absence of carbon dioxide, appears to decrease as the temperature rises. When appreciable quantities of carbon dioxide are present in the vapour phase in contact with solid magnesium carbonate and solutions of other salts, there is a marked tendency towards conditions of false equilibrium. J. C. P.

Zinc Peroxide. BASIL B. KURILOFF (*Compt. rend.*, 1903, 137, 618—619).—The author claims that he has already indicated (*J. Russ. Phys. Chem. Soc.*, 1900, 22, 180) that by the oxidation of zinc oxide with hydrogen peroxide intermediate oxidation products of the type described by de Forcrand (Abstr., 1902, ii, 322 and 606) as zinc peroxides are obtained. He asserts, however, that these substances are not definite compounds, and that only one zinc peroxide, $\text{ZnO}_2 \cdot \text{Zn}(\text{HO})_2$, has so far been definitely proved to exist.

T. A. H.

Double Salts of Cadmium Iodide and Bromide. JOSEF M. EDER (*Zeit. anorg. Chem.*, 1903, 36, 412—413).—A list of double salts of cadmium iodide and bromide prepared by the author (*Phot. Korresp. Wien*, 1876, 13, 83) is quoted. Those salts were prepared in Wesselsky's laboratory, but not by Wesselsky, as Grossmann (Abstr., 1903, ii, 146) imagines. A. McK.

New Thallic Potassium Selenate. VALENTINO FORTINI (*L'Orosi*, 1902, 25, 397—399).—The author has prepared double salts having the following compositions: $\text{Ti}_2(\text{SeO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$ and



These are similar to the corresponding double sulphates described by Piccini and the author (Abstr., 1902, ii, 607).

T. H. P.

Two New Double Halogen Salts. B. GOSSNER (*Zeit. Kryst. Min.*, 1903, 38, 501—503).—A concentrated solution of ammonium iodide dissolves an appreciable amount of cuprous iodide, and the solution deposits orthorhombic crystals of cuprous ammonium iodide, $\text{CuI} \cdot \text{NH}_4\text{I} \cdot \text{H}_2\text{O}$.

A solution of manganous chloride containing excess of magnesium

chloride deposits large, pale red, hexagonal crystals of magnesium manganous chloride, $2\text{MgCl}_2, \text{MnCl}_2, 12\text{H}_2\text{O}$.

Crystallographic descriptions of these are given.

L. J. S.

Complete Separation in the Series of the Rare Earths. GEORGES URBAIN and HENRI LACOMBE (*Compt. rend.*, 1903, 137, 792—794).—By taking advantage of the isomorphism that exists between bismuth magnesium nitrate and the corresponding double salts of magnesium and the metals of the rare earths (this vol., ii, 43), the authors have effected for the first time a complete separation in the series of the rare earths. Thus, when a solution of bismuth magnesium nitrate and the double nitrate of magnesium and the earth rich in samarium is fractionally crystallised, the first few fractions contain all the rare earth, whilst from a solution of bismuth magnesium nitrate and the double nitrate of magnesium and the rare earth rich in gadolinium (and poor in samarium) the rare earth is found in the last crystalline fractions.

M. A. W.

Properties of the Aluminium-Tin Alloys. W. CARRICK ANDERSON and GEORGE LEAN (*Proc. Roy. Soc.*, 1903, 72, 277—284. Compare Heycock and Neville, *Trans.*, 1890, 57, 376; Gautier, *Abstr.*, 1896, ii, 602, 646).—The liquidus curve or freezing point curve slopes gradually downwards from the freezing point of aluminium until a mixture is reached containing about 25 per cent. of aluminium. From all mixtures containing from 17 to 25 per cent. of aluminium the initial separation of solid takes place practically at the same temperature, namely, 561° . Thereafter the curve falls rapidly to a eutectic point at $228-228.5^\circ$ and 0.5 per cent. of aluminium. From the flattening of the liquidus curve referred to above, the authors infer the existence of the compound AlSn (18.5 per cent. aluminium).

All the alloys examined liberate hydrogen from water, and a polished surface exposed to moist air is rapidly pitted. Examination of polished surfaces after water corrosion shows that the action begins round the edge of the areas occupied by the aluminium-rich constituent.

The microscopic structure of the alloys is illustrated by a few photographs. In alloys containing more than 0.5 per cent. of aluminium, two constituents are always visible, the substance which crystallised primarily and the eutectic mixture. By annealing the alloys, the constituent of higher melting point can be made to segregate into patches.

J. C. P.

Compound of Aluminium Sulphate with Sulphuric Acid. E. BAUD (*Compt. rend.*, 1903, 137, 492—494).—When bauxite or aluminium hydroxide is boiled with sulphuric acid previously diluted with its own weight of water, there is formed, when the concentration of the acid reaches 75 per cent., the additive compound, $\text{Al}_2\text{O}_3, 4\text{SO}_3, 4\text{H}_2\text{O}$ (compare Deville, *Ann. Chim. Phys.*, 1860, [iii], 61, 309). This crystallises in colourless needles, dissolves slowly in cold water, and more rapidly on warming. It is also formed when aluminium sulphate is dissolved in sulphuric acid at $110-120^\circ$.

T. A. H.

Crystalline Form of Indium, and its Position in the Periodic System. A. SACHS (*Zeit. Kryst. Min.*, 1903, 38, 495—496).—Electrolytically prepared crystals of indium are regular octahedra. This supports the present reference of indium to the aluminium group rather than to the zinc group, crystals of aluminium being cubic while those of zinc are hexagonal.

L. J. S.

Stimulating or Paralysing Influences Acting on Manganese regarded as a Metallic Enzyme. AUGUSTE TRILLAT (*Compt. rend.*, 1903, 137, 922—924).—The behaviour of manganous salts as metallic enzymes was examined by measuring the volume of oxygen absorbed in a given time by a definite quantity of gallic acid, quinol, pyrogallol, or tannin, in the presence of a manganous salt (chloride, sulphate, or acetate); under these conditions, the manganous salts only become active in the presence of an alkali hydroxide or a salt of an alkaline earth, the increase in the rate of oxidation being proportional to the quantity of alkali hydroxide present, whilst for the same quantity of alkali hydroxide an increase in the quantity of the manganous salt beyond a certain limit has a paralysing effect. Certain substances, such as arsenic acid, mercuric chloride, prussic acid, and hydrogen sulphide, which act as poisons on organisms, have the effect of retarding the reaction.

M. A. W.

A Complex Double Salt of Manganous Acid and Tungstic Acid. ALEXANDER JUST (*Ber.*, 1903, 36, 3619—3622).—When a solution of manganous sulphate is added to a boiling solution of sodium tungstate, manganous tungstate is precipitated. Sodium persulphate is now added, and the solution is boiled for 15 minutes, the volume being kept constant. The dark red solution is filtered from a small quantity of manganese dioxide, and, after a time, red crystals of the colour of potassium dichromate separate. The composition of the salt is represented by the formula $3\text{Na}_2\text{O} \cdot 5\text{WO}_3 \cdot \text{MnO}_2 \cdot 18\text{H}_2\text{O}$, derived from quadrivalent manganese. Solutions of the salt decompose slowly in the cold, rapidly on heating, with deposition of manganese dioxide; it can, however, be crystallised from solutions of sodium tungstate. It may be regarded as a double salt of sodium manganotetratungstate and sodium tungstate, $\text{Mn}(\text{WO}_4\text{Na})_4 \cdot \text{Na}_2\text{WO}_4$. Most metallic salt-solutions yield precipitates. The polytungstates and metatungstates form similar complex salts, which will be further investigated.

C. H. D.

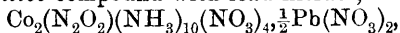
Behaviour of Aqueous Salt Solutions towards Iron Powder. PAUL N. RAIKOW and O. GOWORUCHIN-GEORGIEV (*Chem. Zeit.*, 1903, 27, 1192—1194).—Nitrites, chlorates, bromates, iodates, and chromates, and all those salts the corresponding acids of which form an iron salt insoluble in water, do not form with iron powder an iron salt which is soluble in water. All normal salts of metals of the alkalis and alkaline earths, and those acid salts which possess a distinct alkaline reaction, behave similarly. Soluble iron salts, on the other hand, are formed by the action of iron powder on the normal salts of the heavy metals, zinc, cadmium, silver, copper, &c., on ammonium salts and on those acid salts which have an acid reaction.

A. McK.

Occurrence of Iron in Sulphur. RUDOLF VON HASSLINGER (*Monatsh.*, 1903, 24, 729—736. Compare Biltz and Preuner, Abstr., 1902, ii, 132).—All naturally occurring sulphurs and commercial sulphurs, even those marked "sulph. puriss. cryst.," contain an impurity which is soluble in solvents which dissolve sulphur and is partly volatile with sulphur. On distillation of sulphur, the impurity is partly decomposed, leaving a black residue which consists of a compound of carbon and iron, has a greater sp. gr. than sulphur, is insoluble in sulphur solvents, and when heated in air burns with formation of ferric oxide. This black residue is not identical with Magnus's "black sulphur" (Knapp, Abstr., 1891, 877). Sulphur free from the impurity is obtained on careful oxidation of purified hydrogen sulphide. The impurity is formed on distilling this sulphur with iron and a hydrocarbon, but not with iron alone. G. Y.

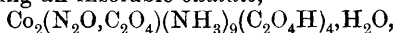
Pentamminenitrosocobalt Salts. JULIUS SAND and OTTO GENSSLER (*Annalen*, 1903, 329, 194—209. Compare Abstr., 1903, ii, 549).—This paper is a more detailed account of the work previously published (*loc. cit.*); it contains the following additional facts. The nitrate of the red series of pentamminenitrosocobalt salts is slowly oxidised in aqueous solution to xanthonitrate (pentamminenitritocobalt nitrate) which is obtained in yellow crystals; by treatment with cold 68 per cent. nitric acid, the nitroso-compound is converted into pentamminenitratocobalt nitrate, $\text{Co}[\text{N}_2\text{O}(\text{NO}_3)_2](\text{NH}_3)_{10}(\text{NO}_3)_4$, no nitrous oxide being evolved.

Of the additive products of the red nitrate, the following are described: the *additive* compound with lead nitrate,



forms lustrous, yellowish-red needles. With potassium iodide in the presence of nitric acid, the *salt*, $\text{Co}_2(\text{N}_2\text{O}_2)(\text{NH}_3)_{10}(\text{NO}_3)_4 \cdot 2\text{HI}$, is obtained in well-formed, brownish-yellow crystals. When the nitrate is treated with a concentrated solution of potassium iodide in the absence of nitric acid, the double *salt*, $\text{Co}_2(\text{N}_2\text{O}_2)(\text{NH}_3)_{10}(\text{NO}_3)_2\text{I}_2 \cdot \text{KI}$, is obtained as a very soluble, brownish-red solid.

The corresponding pentamminenitrosocobalt sulphate reacts with oxalic acid, yielding an insoluble *oxalate*,



which crystallises in pale red, prismatic needles; from the mother liquor, alcohol precipitates the purple *pentamminesulphatocobalt sulphate*, $\{\text{Co}[(\text{SO}_4)(\text{NH}_3)_5]\}_2\text{SO}_4 \cdot \frac{1}{2}\text{C}_2\text{O}_4\text{H}_2$, which is very soluble in water. The red sulphate is decomposed by fuming hydrochloric acid, the *chloride*, $\text{CoCl}(\text{NH}_3)_5\text{Cl}_2$, being deposited as a purple-red precipitate. Concentrated sulphuric acid effects a similar decomposition, nitrous oxide being set free quantitatively. K. J. P. O.

Hydrates of Nickel Sulphate and Methyl Alcohol. CORNELIS A. LOBRY DE BRUYN (*Rec. trav. chim.*, 1903, 22, 407—420. Compare Abstr., 1893, 244, and 1903, ii, 651).—The author has determined the solubilities of the various hydrates of nickel sulphate in methyl alcohol, water, and mixtures of these two solvents. Since solutions of hydrated nickel sulphate in methyl alcohol are

supersaturated with regard to the salt $\text{NiSO}_4 \cdot 3\text{H}_2\text{O} \cdot 3\text{MeOH}$, the solutions were prepared by gradual diffusion without external mechanical agitation. The amount of salt in solution was determined by precipitating the nickel as oxide. The following new hydrates have been obtained. Nickel sulphate hexahydrate (β -form) separates from a concentrated solution of nickel sulphate in methyl alcohol on the addition of $1/4$ to $1/2$ its volume of water. This hydrate is greener in colour than the ordinary α -hexahydrate, into which it appears to be slowly converted when kept. Nickel sulphate tetrahydrate was obtained by crystallisation from a solution of the heptahydrate in sulphuric acid of sp. gr. 1.4 (compare Steele and Johnson, *Trans.*, 1904, 85, 113).

The results of the solubility determinations, which are tabulated in the original, show that the heptahydrate is most soluble in methyl alcohol and the tetrahydrate least soluble; of the two hexahydrates, the β -form is the more soluble. The differences in solubility shown by the hydrates are less marked or disappear entirely with mixtures of methyl alcohol and water. For all the hydrates, the solubility reaches a minimum in mixtures containing 80 per cent. of methyl alcohol and 20 per cent. of water.

When excess of the heptahydrate is boiled with methyl alcohol, the resulting solution contains 18.9 per cent. of nickel sulphate, and on cooling retains 12.8 per cent., the deposited salt consisting of the β -hexahydrate. When excess of the α -hexahydrate is boiled with methyl alcohol, 22.1 per cent. of nickel sulphate dissolves; this solution deposits on cooling 20.1 per cent. of a mixture of the original hexahydrate with the compound $\text{NiSO}_4 \cdot 3\text{H}_2\text{O} \cdot 3\text{MeOH}$. The latter is best obtained by the addition of small quantities of water to solutions of nickel sulphate in methyl alcohol. It forms crystalline crusts, and on exposure to air rapidly loses methyl alcohol. The salt is dissociated when placed in mixtures of methyl alcohol and water containing more than 15 per cent. of the latter. It is more soluble in ethyl alcohol than in methyl alcohol.

T. A. H.

Nickelammonium Hydroxide. G. STARCK (*Ber.*, 1903, 36, 3840. Compare Bonsdorff, *Abstr.*, 1903, ii, 598).—The solubility of nickelous hydroxide in ammonium hydroxide has been determined in the following values obtained:

| | | |
|------------------------|----------------|------------------|
| Conc. of ammonia | 1 <i>N</i> | 2 <i>N</i> |
| Conc. of nickel | 0.014 <i>N</i> | 0.036 <i>N</i> . |

J. J. S.

Preparation of Metallic Thorium and Yttrium and their Alloys. SIEMENS & HALSKE, AKT.-GES. (D.R.-P. 146503).—Mixtures of thorium or yttrium salts with salts of more fusible metals, as tin, lead, zinc, antimony, aluminium, or copper, are reduced by sodium vapour or by sodium hydroxide and carbon. Or the fluorides of the rare earth metals may be heated with metallic tin or lead. In either case an alloy is obtained, from which the pure thorium or yttrium may be extracted electrolytically or by means of appropriate chemical solvents.

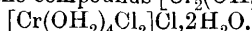
C. H. D.

Radioactive Thorium. FRITZ ZERBAN (*Ber.*, 1903, 36, 3911—3912. Compare *Abstr.*, 1903, ii, 732).—All minerals, for example monazite from Bahia, South Carolina, and Australia, which give radioactive thorium, contain, contrary to Barker's statement, small quantities of uranium. Minerals such as gadolinite from Sotersdal, and Norwegian orthite and yttrite, which are free from uranium, give inactive thorium. W. A. D.

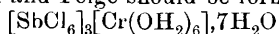
Electrolytic Preparation of Vanadium and its Alloys. GUSTAV GIN (*Zeit. Elektrochem.*, 1903, 9, 831—832).—The electrolyte consists of fused calcium fluoride, to which some fluoride of iron is added. The anode consists of a mixture of vanadium trioxide and carbon, compressed and roasted in the way used in making anodes of carbon alone, the cathode is a bath of fused steel. In making alloys containing more than 25 per cent. of vanadium, a current density of 2 amperes per sq. cm. at the anode and 6 amperes per sq. cm. at the cathode is used; 11 to 12 volts are required. The author supposes that iron fluoride is electrolysed, the fluorine liberated reacting with the anode, thus: $6F + V_2O_3 + 3C = 2VF_3 + 3CO$; the vanadium fluoride dissolves in the fused calcium fluoride and is then itself electrolysed. T. E.

Compounds of Quadrivalent Vanadium. II. IWAN KOPPEL and R. GOLDMANN (*Zeit. anorg. Chem.*, 1903, 36, 281—301. Compare this vol., i, 7).

Constitution of the Double Salts of Antimony Pentachloride and Chromium Chloride. PAUL PFEIFFER (*Zeit. anorg. Chem.*, 1903, 36, 349—354).—Weinland and Feige (*Abstr.*, 1903, ii, 218) have prepared various double salts of antimony pentachloride, which they regard as derivatives of metachloro-, pyrochloro- and orthochloro-antimonic acids respectively. The author shows that the salt $CrCl_3 \cdot SbCl_5 \cdot 10H_2O$ is not a derivative of the ortho- acid. According to Weinland and Feige, the salt $CrCl_3 \cdot 3SbCl_5 \cdot 13H_2O$ crystallises in violet-gray needles, whilst the salt $CrCl_3 \cdot SbCl_5 \cdot 10H_2O$ forms green leaflets; the latter salt was obtained by the author in the form of dark green crystals. The solutions obtained in both cases, however, when the antimony is removed by hydrogen sulphide, are not identical, since in the one case a violet solution and in the other a green solution is formed. These solutions are identical with those of the compounds $[Cr_2(OH_2)_6]Cl_3$ and



The salts of Weinland and Feige should be formulated thus:



(violet), and $[SbCl_6][Cr(OH_2)_4Cl_2] \cdot 6H_2O$ (green). In the violet salt, the chlorine atoms are in the negative radicle, but in the green salt they are divided between both radicles. Those salts are analogous to the iron salts, $[SbCl_3]Fe \cdot 8H_2O$ and $[SbCl_6][Fe(OH_2)_4Cl_2] \cdot 4H_2O$.

It is further pointed out that the large majority of chlorine salts containing quinquevalent antimony are derivatives of Werner's type, $[SbCl_6]M'$. A. McK.

Kermes Mineral. J. BOUGAULT (*Compt. rend.*, 1903, 137, 794).—Kermes mineral owes its therapeutic value to antimony oxide which is formed by the action of the acids of the stomach on the antimony sulphide and sodium pyroantimonate contained in the compound (compare Feist, Abstr., 1902, ii, 507). M. A. W.

Bismuth Oxychloride and Oxybromide. WALTER HERZ (*Zeit. anorg. Chem.*, 1903, 36, 346—348).—Bismuth oxychloride, prepared by the addition of water to bismuth trichloride, does not contain water of crystallisation. When heated, it gradually turns yellow and in part brown; when cooled, the original white colour is not restored. When heated, it forms a slight sublimate of tiny, glistening crystals. It is superficially blackened at the ordinary temperature under the influence of light. Bismuth oxybromide closely resembles the oxychloride. A. McK.

Fusibility of Mixtures of Sulphur and Bismuth. HENRI PÉLABON (*Compt. rend.*, 1903, 137, 648—550).—Bismuth sulphide and bismuth when melted form a homogeneous liquid the points of solidification of which lie between that of bismuth sulphide (685°) and bismuth (255°). The fusibility curve of the mixtures obtained by plotting as ordinates solidification temperatures determined from the cooling curves against the percentage composition in sulphur of the corresponding mixtures as abscissæ, shows three straight portions with two angular points, forming a broken line concave to the abscissa. One of the angular points is at the temperature of 435° , the solidification temperature of a mixture containing one-sixteenth of an atom of sulphur to 1 atom of bismuth; the other angular point is at 685° , the solidification temperature of bismuth sulphide, BiS ; beyond this point the curve can only be traced a short distance to a point corresponding with a mixture of four atoms of sulphur with three of bismuth, because when the sulphur exceeds this proportion, the excess does not unite with the mixture. These results agree with those previously obtained by the author in studying the action of hydrogen on bismuth sulphide (Abstr., 1901, ii, 165). M. A. W.

Fusibility of Mixtures of Bismuth Monosulphide and Silver Sulphide; and of Bismuth Monosulphide and Antimony Sulphide. HENRI PELABON (*Compt. rend.*, 1903, 137, 920—922).—The freezing point curve of mixtures of bismuth monosulphide and silver sulphide, obtained by plotting the solidification temperatures as ordinates and the percentage of silver sulphide in the mixture as abscissæ, consists of five straight lines showing two minima and one maximum; the two minima correspond with the two eutectic mixtures containing Ag_2S 6.5 and 72 per cent. respectively, and melting at 648° and 585° ; the maximum corresponds with the compound $\text{Ag}_2\text{S}, 4\text{BiS}$ and melts at 750° . Between the maximum and second minimum the curve shows an angular point corresponding with a mixture in which the two sulphides are present in the proportion indicated by the formula $\text{Ag}_2\text{S}, 2\text{BiS}$.

The freezing point curve of mixtures of antimony sulphide and bismuth monosulphide consists of three straight lines inclined at angles very little removed from 180° ; the two angular points correspond with mixtures in which the sulphides are present in the proportions indicated by the formulæ $3\text{BiS}, \text{Sb}_2\text{S}_3$ (m. p. 632°) and $\text{BiS}, 4\text{Sb}_2\text{S}_3$ (m. p. 591°) respectively.

M. A. W.

A Series of Compounds of Bismuth. GEORGES URBAIN and HENRI LACOMBE (*Compt. rend.*, 1903, 137, 568—569).—Bismuth nitrate forms a series of double salts having the general formula $3\text{M}''(\text{NO}_3)_2, 2\text{Bi}(\text{NO}_3)_3, 24\text{H}_2\text{O}$ (in which M'' represents magnesium, zinc, nickel, cobalt, or manganese), isomorphous with the double nitrates of the rare earths and the corresponding metal of the magnesium series. The double salts effloresce in dry air; they are deliquescent, that of manganese being the most, and those of nickel and magnesium the least so; and like all bismuth salts they are decomposed by water.

Magnesium bismuth nitrate is colourless, melts with decomposition at 71° , and has the sp. gr. 2.32 at $16^\circ/16^\circ$. *Zinc bismuth nitrate* is colourless, melts and decomposes at 67.5° , and has the sp. gr. 2.75 at $16^\circ/16^\circ$. *Nickel bismuth nitrate* is green, melts without decomposition at 69° , and has the sp. gr. 2.51 at $16^\circ/16^\circ$. *Cobalt bismuth nitrate* is red, and more orange in tint than the corresponding salt of neodymium; it melts without decomposition at 58° and has the sp. gr. 2.48 at $16^\circ/16^\circ$. *Manganese bismuth nitrate* is pale red. It is the most unstable of the series and does not exist in contact with the solid phase of either constituent; it melts without decomposition at $43\text{--}44^\circ$ and has the sp. gr. 2.42 at $16^\circ/16^\circ$.

M. A. W.

Colloidal Gold. Absorption Phenomena and Allotropy. J. C. BLAKE (*Amer. J. Sci.*, 1903, [iv], 16, 381—387).—"Yellow gold" is golden in reflected light and blue in transmitted light; "blue gold" is dark bronze in reflected light and blue in transmitted light; "red gold" is light golden in reflected light and red in transmitted light. Red gold solution was prepared by pouring an ethereal solution of gold chloride (dried at 170°) into water in which ether and acetylene had been dissolved. Solutions made in this manner were precipitated by solutions of various barium salts and the coagulum analysed for gold, barium, and carbon. When the gold chloride was not all reduced, the colloidal gold was separated in a spongy form by the barium salts. Very little of the barium compound is retained by the gold under those conditions. When the gold chloride is all reduced, the colloidal gold was separated by the solution of barium salt in the non-coherent blue form. So long as the solution is even slightly acid, traces of barium are retained by the gold, but when the solution is alkaline, an appreciable amount of barium is retained by the gold, a result in accordance with van Bemmelen's equation for absorption from solution by porous solids, $C''_{\text{KOH}} = f(C'_{\text{K}_2\text{SO}_4}, C'_{\text{SO}_3})$, where C''_{KOH} represents the concentration of the base in the liquid retained by the solid, and C' the concentrations of the given substance in the supernatant liquid.

Absorption phenomena are not markedly concerned in the colour changes effected by electrolytes in red gold solutions or in the subsequent precipitation of the spongy or the blue gold. A. McK.

Gold Fluoride. VICTOR LENHER (*J. Amer. Chem. Soc.*, 1903, 25, 1136—1138).—Moissan states that at a red heat, gold is attacked by fluorine, a yellow hygroscopic substance being formed which readily decomposes into gold and fluorine. The author finds that gold oxide is not dissolved by hydrofluoric acid. When aqueous solutions of gold chloride and silver fluoride are mixed, gold hydroxide is quantitatively deposited along with silver chloride. It is supposed that gold fluoride is incapable of existence in the presence of water.

A. McK.

Oxidisability of Platinum. LOTHAR WÖHLER (*Ber.*, 1903, 36, 3475—3502. Compare Engler and Wöhler, *Abstr.*, 1902, ii, 127).—Platinum black absorbs 2.3 per cent. of oxygen when heated at temperatures up to 280° in an atmosphere of pure oxygen, equilibrium only being attained after several weeks. When such oxidised platinum black is extracted with dilute hydrochloric acid in an atmosphere of carbon dioxide, 12—18 per cent. of the platinum passes into solution in the form of platinous chloride. If the whole of the oxygen were combined in the form of soluble platinous oxide, 25 per cent. of platinum would dissolve, but a part of the oxygen forms an insoluble oxide, as is shown by the oxidising action of the residual metal on a solution of diphenylamine in sulphuric acid. Mond, Ramsay, and Shields (*Abstr.*, 1898, ii, 599) also found that the heat of absorption of oxygen by platinum black corresponds closely with the heat of formation of platinous hydroxide. The oxidising action of platinous hydroxide on potassium iodide, arsenious acid, organic compounds, &c., is identical with that of platinum black.

Platinous hydroxide only begins to decompose when heated at about 400° in a vacuum or in carbon dioxide; platinic hydroxide passes into the platinous compound below 300°, but the less water is present the more slowly the decomposition goes on.

Platinum sponge, and even thin platinum foil, absorb oxygen with superficial blackening at 420—450°, the product containing as much as 43 per cent. of anhydrous platinous oxide. Hydrochloric acid extracts only traces of platinum, but the addition of a minute quantity of platinous chloride greatly hastens solution. Platinic chloride has no such action.

Catalytic oxidation by means of platinum may take place in two ways, in accordance with the presence or absence of water. In the first case, Pt_xO_y passes into $Pt_x(O_2)_y$; in the second, the reaction $Pt + 2H_2O + O_2 = Pt(OH)_2 + H_2O_2$ takes place. Platinum can also, in the absence of oxygen, decompose water with the evolution of hydrogen, for example, in solutions of cyanides, platinum being dissolved as complex ions. The dissolution of platinum is very rapid when hydrogen peroxide is added to the cyanide solution.

C. H. D.

Constitution of Ruthenium Potassium Nitrosochloride in Aqueous Solution. S. C. LIND (*J. Amer. Chem. Soc.*, 1903, 25, 928—932).—Determinations of the electrical conductivity of ruthenium potassium nitrosochloride showed that aqueous solutions of the substance in varying concentrations are perfectly stable; in two weeks, the conductivity of the solutions did not change. The values for the molecular conductivity were nearly identical with those for potassium platinichloride. The values for the lowering of the freezing point of water indicated that the salt is partially dissociated into three ions, the value for van't Hoff's coefficient varying from 2.52 to 2.72 in 1/20 to 1/70 molar solution respectively. The degree of dissociation, deduced from the freezing point experiments, is in close agreement with the value for potassium platinichloride and is in accordance with the value obtained from the conductivity experiments. The direction of migration of the coloured ions showed that the ruthenium was present in the negative ion.

A. McK.

Mineralogical Chemistry.

Italian Petroleum. II. LUIGI BALBIANO and P. ZEPPA (*Gazzetta*, 1903, 33, ii, 42—50. Compare Balbiano and Palladini, *Abstr.*, 1902, ii, 567).—The fractions of the petroleum from Valleja, boiling between 87° and 102°, contains no olefines, but a study of its oxidation products indicates the presence of benzene, cyclohexane, methylcyclopentane, and 1:3-dimethylcyclopentane. T. H. P.

Hydrocarbons in Louisiana Petroleum. CHARLES E. COATES and ALFRED BEST (*J. Amer. Chem. Soc.*, 1903, 25, 1153—1158).—An examination of a specimen of Louisiana petroleum showed that hydrocarbons of the series C_nH_{2n-2} and C_nH_{2n-4} were the main constituents. A. McK.

Mineralogical Notes. CHARLES H. WARREN (*Amer. J. Sci.*, 1903, [iv], 16, 337—344).—*Native Arsenic from Arizona*.—This was found as reniform masses lining a cavity in metamorphosed dolomitic limestone at Washington Camp, Santa Cruz Co. It contains a small amount of antimony and a trace of sulphur.

Anthophyllite with Fayalite from Rockport, Massachusetts.—A second large lenticular mass of fayalite (Fe_2SiO_4) has been found in the pegmatite of Rockport (*Abstr.*, 1896, ii, 373). It encloses numerous grains of magnetite, and, where it is bordered by the quartz of the pegmatite, it is surrounded by a zone of fibrous anthophyllite. The anthophyllite is white to light brown in colour; it contains only traces of aluminium and magnesium, and appears to be pure iron antho-

phylite (FeSiO_3); it has evidently been derived from the fayalite and quartz.

Cerussite and Phosgenite from Colorado.—Massive greyish-white to yellow cerussite from Isle, Custer Co., is remarkable in containing strontium isomorphously replacing lead; analysis gave:

| CO_2 | PbO. | SrO. | BaO, CaO. | Alkalis, FeO. | Total. | Sp. gr. |
|---------------|-------|------|-----------|---------------|--------|---------|
| 17.02 | 79.59 | 3.15 | nil | traces | 99.76 | 6.409 |

The cerussite surrounds, and appears to be an alteration product of, clear brown phosgenite; the latter contains no strontium.

L. J. S.

Eglestonite, Terlinguaite, and Montroydite, New Mercury Minerals from Terlingua, Texas. ALFRED J. MOSES (*Amer. J. Sci.*, 1903, [iv], 16, 253—263).—The three new minerals occur together and in association with cinnabar, native mercury, calomel and calcite at Terlingua, Brewster Co., Texas. BENJAMIN F. HILL, in an accompanying paper (*ibid.*, 251—252), describes the mode of occurrence of the mercury ores in this district.

Eglestonite.—The minute cubic crystals have the rhombic dodecahedron as the predominating form; they have a brilliant adamantine to resinous lustre, and their brownish-yellow colour quickly alters to black on exposure to light. The mean (I) of several analyses by J. S. McCord gives the formula $\text{Hg}_6\text{Cl}_3\text{O}_2$. The crystals, when heated, volatilise as mercury and mercuric chloride, and the loss in weight was assumed to be oxygen.

Terlinguaite.—The monoclinic crystals [$a:b:c=0.5306:1:2.0335$; $\beta=74^\circ 16'$] are bright sulphur-yellow, and on exposure to light very slowly alter to olive-green. They are more readily soluble in nitric acid than are crystals of eglestonite. The mean (II) of several analyses by McCord gives the formula Hg_2ClO .

Montroydite.—This is usually found as a velvety incrustation of orange-red needles; larger transparent crystals resemble realgar in colour; the lustre is adamantine to vitreous. The crystals are orthorhombic [$a:b:c=0.63797:1:1.1931$]. Analysis III shows the mineral to be mercuric oxide, HgO .

| | Hg. | Cl. | O. | Total. | Sp. gr. | Hardness. |
|------|-------|------|------|--------|---------|-----------|
| I. | 89.56 | 7.93 | 2.43 | 99.92 | 8.327 | 2—3 |
| II. | 88.24 | 7.89 | 3.47 | 99.60 | 8.725 | 2—3 |
| III. | 92.87 | — | 7.13 | 100.00 | — | < 2 |

A crystallographic description is given of the calomel which is associated with these minerals. An undetermined yellow mineral, which is perhaps an orthorhombic oxychloride of mercury, is briefly described.

L. J. S.

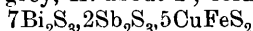
Formula of Bornite. BERNARD J. HARRINGTON (*Amer. J. Sci.*, 1903, [iv], 16, 151—154).—Analyses of massive bornite from various Canadian localities (I—V), and of material crystallised in rhombic dodecahedra from Bristol, Connecticut (VI), all agree with the formula

Cu_5FeS_4 . The usually accepted formula, $\text{Cu}_3\text{FeS}_3 (= \text{Cu}_5\text{FeS}_4 + \text{CuFeS}_2)$, was based, in 1839, on analyses of Cornish crystals, but these are always impure and usually contain a nucleus of chalcopyrite (CuFeS_2). New analyses of Cornish crystals are given under VII and VIII.

| | I. | II. | III. | IV. | V. | VI. | VII. | VIII. | Cu_5FeS_4 . |
|---------|--------|-------|-------|--------|-------|-------|-------|-------|-----------------------------|
| Cu ... | 63·55 | 62·78 | 62·73 | 63·34 | 63·18 | 63·24 | 57·71 | 57·68 | 63·27 |
| Fe ... | 10·92 | 11·28 | 11·05 | 10·83 | 11·28 | 11·20 | 13·89 | 15·11 | 11·18 |
| S ... | 25·63 | 25·39 | 25·79 | 25·54 | 24·88 | 25·54 | 27·17 | 26·46 | 25·55 |
| Insol. | — | 0·30 | — | 0·38 | 0·24 | — | — | — | — |
| Total | 100·10 | 99·75 | 99·57 | 100·09 | 99·58 | 99·98 | 98·77 | 99·25 | 100·00 |
| Sp. gr. | 5·085 | 5·055 | 5·090 | 5·029 | — | 5·072 | — | — | — |

L. J. S.

Tasmanian Minerals. W. F. PETTERD (*Rep. Secr. Mines, Tasmania*, for 1901—2, 1902, 288—303; *Papers and Proc. R. Soc. Tasmania*, for 1902, 1903, 18—33).—Notes are given of eighty mineral species, half of which have not been previously recorded, from Tasmania. Analyses, mostly by S. Pascoe and O. E. White, are given of the following: I, Arsenopyrite, in minute crystals from Ringville. II, Bournonite, in well-developed crystals. III, Dufrenoyite, in large, well-developed, orthorhombic crystals on chalybite from Dundas. IVa and b, *Histricite*, an apparently new mineral, from Ringville. This occurs with pyrites, chalcopyrite, tetrahedrite, and bismuthinite as radiating groups of orthorhombic crystals of prismatic habit and striated longitudinally. Colour and streak steel-grey, H. about 2; formula:



[suggesting a mixture]. Va, Jamesonite, from Magnet Mine; Vb, From Mount Bischoff. VI, Stromeierite, massive, from Mt. Lyell Mine. VII, Tennantite, from Mt. Lyell Mine. VIII, Tetrahedrite, from Mt. Read.

| | S. | Bi. | Sb. | As. | Pb. | Cu. | Ag. | Fe. | Insol. | Total. |
|-------|-------|-------|---------|-------|-------|-------|-------|-------|-------------|--------|
| I. | 21·48 | — | about 2 | 43·20 | — | — | — | 32·95 | — | 99·63 |
| II. | 13·62 | — | 28·68 | — | 42·39 | 11·93 | — | 1·97 | — | 98·40 |
| III. | 21·79 | — | 8·53 | 21·60 | 32·88 | 9·08 | 0·22 | 6·42 | — | 100·52 |
| IVa. | 24·05 | 55·93 | 10·08 | — | — | 6·86 | — | 5·18 | — | 102·10 |
| IVb. | 23·01 | 56·08 | 9·33 | — | — | 6·12 | — | 5·44 | — | 99·98 |
| Va. | 17·51 | — | 21·48 | 2·44 | 40·82 | — | 0·12 | 4·91 | 11·51 | 98·85 |
| Vb. | 17·82 | — | 26·74 | trace | 32·08 | — | 0·12 | 5·56 | 14·28 | 96·60 |
| VI. | 38·27 | — | trace | 3·17 | 1·60 | 32·46 | 13·80 | 19·26 | — | 98·66 |
| VII. | 30·77 | — | 17·10 | 13·82 | — | 16·17 | 0·54 | 16·39 | — | 94·79 |
| VIII. | 27·21 | — | ? | 2·69 | — | 29·76 | 9·82 | 4·56 | (Au=0·0019) | |

IX, Dundasite, from Dundas, previously described as a hydrated carbonophosphate of lead and aluminium. The ferric oxide is probably present as an impurity, and a trace of phosphoric acid is due to the presence of admixed pyromorphite. Dundasite is also mentioned as occurring at Mt. Read in association with cerussite and gibbsite [and it may prove to be a mixture of these.—L. J. S.]. X, Knoxvilleite (?), as a pale green, granular mineral from Salisbury. Associated with this is another sulphate occurring as large, felted masses of short, silky fibres; this is readily soluble in water and gave analysis XI; it is

provisionally named *sclerospathite*. XII, Cerussite, yellowish-green, from Dundas; analysis by J. C. H. Mingaye.

| | PbO. | Al ₂ O ₃ . | Fe ₂ O ₃ . | Cr ₂ O ₃ . | SO ₃ . | H ₂ O. | CO ₂ . | Loss on ignition. | Insol. | Total. |
|------|-------|----------------------------------|----------------------------------|----------------------------------|-------------------|-------------------|-------------------|----------------------|--------|--------|
| IX. | 41·86 | 26·06 | 5·50 | — | — | 28·08 | — | — | — | 101·50 |
| X. | — | 2·48 | 15·86 | 8·47 | 30·32 | — | — | 40·56 | — | 97·59 |
| XI. | — | — | 14·00 | 10·64 | 27·20 | — | — | 39·19 | 10·77 | 101·80 |
| XII. | 83·07 | — | — | trace | — | — | 15·97 | — | 0·62 | 99·66 |

Dolomite, white, from Magnet Mine; analysis by F. O. Hill: CaO, 31·72; MgO, 15·60; Fe, 3·92; Mn, 1·80. L. J. S.

Petterdite, a New Lead Oxychloride. WILLIAM H. TWELVETREES (*Rep. Secr. Mines, Tasmania*, for 1900—1, 1901, 356—357; *Papers and Proc. R. Soc. Tasmania*, for 1900—1, 1902, 51—52).—This new mineral occurs as attached crystals having the form of thin, hexagonal plates, 5—9 mm. across, with quartz, pyrites, and sometimes campylite, in the Britannia Mine, Zeehan, Tasmania. The colour is white; H. = $1\frac{1}{2}$ —2; sp. gr. 7·16. Analysis, by O. E. White, gave:

| PbO. | As ₂ O ₅ . | P ₂ O ₅ . | Sb ₂ O ₃ . | Cl. |
|-------|----------------------------------|---------------------------------|----------------------------------|-----|
| 74·04 | 2·60 | 2·10 | 0·50 | 20 |

L. J. S.

Formation of Dolomite. F. W. PFAFF (*Centr. Min.*, 1903, 659—660. Compare *Abstr.*, 1895, ii, 50).—The frequent occurrence of gypsum with dolomite suggests that the latter may have been formed by the action of carbon dioxide on calcium and magnesium sulphates. Experiments in this direction with gypsum were without result, but with anhydrite dolomite was formed. Dolomite was deposited on the slow evaporation of a solution containing carbon dioxide and calcium and magnesium sulphates, together with calcium, magnesium, and sodium chlorides (the latter influencing the formation of anhydrite). L. J. S.

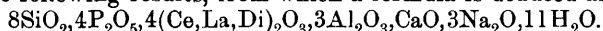
Hydromagnesite and Artinite from Emarese in the Aosta Valley. LUIGI BRUGNATELLI (*Centr. Min.*, 1903, 663—665).—In specimens from the asbestos mines of Emarese, the following minerals were noted: asbestos (tremolite and serpentine), demantoid, aragonite, calcite, hydromagnesite, and artinite. The artinite (*Abstr.*, 1903, ii, 379) occurs as silky tufts (not scales, as stated in the original description) of delicate acicular crystals, and agrees in its characters with the artinite of the Val Lanterna. The hydromagnesite occurs as nodular aggregates of fine scales, the optical characters of which suggest orthorhombic, rather than monoclinic, symmetry. These two minerals are associated together and with corroded calcite, suggesting that they have been derived by the action of solutions of magnesium salts on the calcite. L. J. S.

Alteration of Augite to Carbonates. LUDWIG MILCH (*Centr. Min.*, 1903, 505—509).—The augites of a volcanic rock from Sumatra

have been altered to an aggregate of carbonates with some chlorite. Microscopical examination and microchemical tests proved the presence of three carbonates. Analysis of the portions of the rock soluble in dilute hydrochloric acid and in acetic acid gave: CaO, 3.0; MgO, 2.2; FeO, 1.7; CO₂, 5.4 per cent.; this composition points to calcite, magnesite, and a brown spar. L. J. S.

Identity of Palacheite with Botryogen. ARTHUR S. EAKLE (*Amer. J. Sci.*, 1903, [iv], 16, 379—380).—Palacheite, recently described by the author as a new mineral (*Abstr.*, 1903, ii, 490), is now found to be crystallographically and chemically identical with botryogen. L. J. S.

Erikite and Schizolite from Greenland. O. B. BÖGGILD (*Meddel. om Grönland*, 1903, 26, 91—139).—*Erikite*.—This new mineral was found with arfvedsonite, ægirite, analcite, and natrolite in veins penetrating the nephelite-syenite near Julianehaab. The opaque, brown crystals are orthorhombic ($a:b:c=0.5755:1:0.7579$). Sp. gr. 3.493; H. 5½—6. In thin sections, the crystals are seen to be pseudomorphous, and to consist of an intergrowth of two substances. The predominating substance (erikite) is yellow, strongly refracting, and birefringent, and has the structure of a granular aggregate with a reticular arrangement: in the interspaces of this rectangular network is a colourless and feebly refracting and birefringent mineral, which is probably hydronephelinite. Analysis by Chr. Christensen gave the following results, from which a formula is deduced as,



| SiO ₂ . | P ₂ O ₅ . | (Ce, La, Di) ₂ O ₃ . | ThO ₂ . | Al ₂ O ₃ . | CaO. | Na ₂ O. | H ₂ O. | Total. |
|--------------------|---------------------------------|--|--------------------|----------------------------------|------|--------------------|-------------------|--------|
| 15.12 | 17.78 | 40.51 | 3.26 | 9.28 | 1.81 | 5.63 | 6.28 | 99.67 |

The material analysed being a mixture of two unknown substances, it is impossible to say how far this analysis represents the original composition of the crystals before alteration.

Erikite is placed in a group comprising compounds of silicates, titanates, &c. (mostly metatitanates, &c.), with columbates, tantalates, phosphates, antimonates, &c. (mostly metacolumbates, &c.). In the cubic members (pyrochlore, lewisite, &c.) of this group, the ratio of the acid oxides RO₂:R₂O₅ is equal to or less than 1, whilst in all others it is equal to or greater than 2.

Schizolite (*Abstr.*, 1900, ii, 413).—A new crystallographic examination of this mineral shows it to be anorthic, and to be related to pectolite as rhodonite is to wollastonite. Several types of crystals are described and figured. Sp. gr. 2.971—3.133. Colour, rose-red or dark brown. Material from Kangerdluarsuk gave, on analysis by Chr. Christensen, the following results, agreeing with the formula 9SiO₂, 6R''O, 2(Na, H)₂O.

| SiO ₂ . | TiO ₂ . | Ce ₂ O ₃ . | Y ₂ O ₃ . | FeO. | MnO. | CaO. | Na ₂ O. | H ₂ O. |
|--------------------|--------------------|----------------------------------|---------------------------------|------|------|-------|--------------------|-------------------|
| 51.06 | 0.62 | 0.94 | 1.03 | 2.74 | 9.84 | 22.89 | 9.97 | 0.55 |

L. J. S.

Datolite from Lištic, Bohemia. FR. SLAVÍK and J. FIŠER (*Centr. Min.*, 1903, 229—235).—At Lištic, near Beroun, clay-slate has been altered, at its contact with diabase, to a compact adinole-like rock consisting mainly of datolite; some quartz and a little felspar are also present. Analysis by H. Friedrich gave:

| | | | | | |
|--------------------|--------------------|---------------------------------|---------------------------------------|----------------------------------|------|
| SiO ₂ . | CaO. | B ₂ O ₃ . | FeO, Fe ₂ O ₃ . | Al ₂ O ₃ . | MgO. |
| 44.92 | 25.56 | 17.64 | 3.09 | 3.40 | 0.34 |
| K ₂ O. | Na ₂ O. | H ₂ O. | Total. | Sp. gr. | |
| 3.17 | 0.57 | 1.76 | 100.45 | 2.916 | |

The excess of silica over that required by the datolite formula (Ca[B·OH]SiO₄) is due to the presence of quartz; the low percentage of water suggests that the group OH is partly replaced by the groups OK and ONa. Crevices in the datolite-rock are lined with colourless crystals of datolite, of which a description is given. L. J. S.

Idocrase ("Californite") as an Ornamental Stone. GEORGE F. KUNZ (*Amer. J. Sci.*, 1903, [iv], 16, 397—398).—A compact variety of idocrase occurs abundantly and in large masses in Siskiyou County, California, at a spot ninety miles from Yreka; the associated rock is precious serpentine. It is olive-green to almost grass-green in colour, and takes a fine polish. H. 6½; sp. gr. 3.286. Like the massive idocrase of Piz Longhin in Switzerland, it is thus very similar to jade in appearance. Analysis, by G. Steiger, gave:

| | | | | | |
|--------------------|----------------------------------|----------------------------------|-------------------|--------|-------|
| SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | MnO. | CaO. |
| 35.85 | 18.35 | 1.67 | 0.39 | 0.05 | 33.51 |
| MgO. | TiO ₂ . | P ₂ O ₅ . | H ₂ O. | Total. | |
| 5.43 | 0.10 | 0.02 | 4.47 | 99.85 | |

The material is well suited for the purposes of an ornamental stone, and for it the name "Californite" is proposed. Its occurrence at two other localities in California is noted. L. J. S.

A Peculiar Diopside from Moravicza, Hungary. ERNST WEINSCHENK (*Tsch. Min. Mitt.*, 1903, 22, 363—367).—In a granular limestone from Moravicza were observed large, bright green crystals of garnet, and imperfect crystals of a light red mineral which was determined to be diopside. Approximate measurements of the crystals suggested anorthic symmetry, but the optical characters agree with those of diopside. The following analysis, by Schindelbeck, shows the presence of much lime and manganese oxide, and the absence of alumina and alkalis.

| | | | | | | |
|--------------------|------|------|-------|------|-------------------|----------|
| SiO ₂ . | FeO. | MnO. | CaO. | MgO. | Loss on ignition. | Total. |
| 51.98 | 2.96 | 5.76 | 28.96 | 8.59 | 0.56 | 98.81 |
| | | | | | | L. J. S. |

[Minerals from] the Neighbourhood of Mount Magnitnaia Urals. JÓZEF MOROZEWICZ (*Zeit. Kryst. Min.*, 1903, 38, 201—204; from *Mém. Com. Géol. St. Pétersbourg*, 1901, 18, 1—73; *Résumé*, 74—104).—The district around Mount Magnitnaia, situated on the eastern slopes of the southern Urals, consists of igneous and metamorphic rocks, with some sedimentary rocks and large deposits of iron ores. The following mineral analyses are given: I and II, diopside, isolated from augite-diorite from Mount Atatsch; III, augite; IV, garnet; V, augite; VI—VIII, garnet (melanite); IX, epidote.

The augite of the igneous rocks has been altered to garnet, and this to epidote, the final product being quartz, calcite, and iron ores. The large masses of iron ore are considered to have been formed by this process of alteration rather than by magmatic differentiation.

| | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | FeO | MnO | CaO | MgO | K ₂ O | Na ₂ O | H ₂ O | Total | Sp. gr. |
|-------|------------------|--------------------------------|--------------------------------|-------|------|-------|-------|------------------|-------------------|------------------|--------|---------|
| I. | 51·72 | 1·00 | 2·14 | 5·75 | 0·20 | 23·63 | 13·77 | trace | 1·13 | 0·59 | 99·93 | 3·330 |
| II. | 49·42 | 4·77 | 3·95 | 6·25 | 0·20 | 17·91 | 14·41 | trace | 1·90 | 1·51 | 100·32 | 3·198 |
| III. | 44·16 | 11·72 | 4·40 | 7·25 | 0·35 | 21·98 | 5·44 | 0·82 | 1·11 | 1·58 | 98·81 | 3·311 |
| IV. | 36·89 | 6·22 | 23·49 | 2·23 | 0·42 | 29·97 | trace | — | — | 0·97 | 100·19 | 3·701 |
| V. | 50·65 | 2·26 | 2·42 | 11·20 | 0·60 | 17·87 | 14·37 | trace | 0·82 | 0·58 | 100·77 | 3·196 |
| VI. | 35·28 | 0·40 | 30·31 | 0·28 | 0·46 | 32·93 | trace | — | — | 0·98 | 100·34 | 3·811 |
| VII. | 55·00 | 2·15 | 30·41 | 0·48 | 0·48 | 31·47 | trace | — | — | 1·36 | 100·87 | — |
| VIII. | 35·08 | 8·39 | 21·09 | 1·48 | 0·87 | 32·98 | trace | — | — | 0·69 | 100·58 | 3·682 |
| IX. | 36·58 | 20·62 | 16·68 | 0·37 | 0·20 | 23·29 | 0·24 | — | — | 2·27 | 100·25 | 3·445 |

L. J. S.

Aluminous and Titaniferous Augites. G. BECKER (*Zeit. Kryst. Min.*, 1903, 38, 317—319; from *Sitzungsber. phys.-med. Soc. Erlangen*, 1901, 33, 219—267).—The following augites were subjected to prolonged digestion at 60° in dilute hydrochloric acid, and the soluble (a) and insoluble (b) positions separately analysed. In the soluble portion, SiO₂:Al₂O₃:(Ca,Mg)O=1:1:3½. The results are discussed, and complex structural formulæ given: I, augite from Kilimandjaro; sp. gr. 3·36. II, Augite from Falkenberg, Bohemia; sp. gr. 3·39. III, Augite from Fladungen, Rhön; sp. gr. 3·27.

| | SiO ₂ | TiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | FeO | CaO | MgO | Loss on ignition. | Total. |
|---------|------------------|------------------|--------------------------------|--------------------------------|--------------|-------|-------|----------------------------|--------|
| I. | 44·89 | 2·39 | 3·93 | 2·72 | 10·54 | 22·13 | 12·79 | 0·11 | 99·50 |
| I(a). | 2·36 | 0·745 | 3·875 | — | 0·73 | 4·345 | 2·305 | — | 14·36 |
| I(b). | 42·51 | 1·525 | — | 3·23 | 9·63 | 18·01 | 10·23 | — | 85·135 |
| II(a). | 2·71 | 1·01 | 4·37 | — | 0·86 | 4·80 | 2·61 | — | 16·36 |
| II(b). | 34·51 | 5·58 | 1·76 | 9·56 | — | 20·32 | 10·58 | — | 82·31 |
| III(a). | 2·51 | 2·40 | 4·14 | 2·78 | 6·47 | 5·06 | 2·20 | — | 25·56 |
| III(b). | 21·60 | 6·31 | 3·83 | 12·27 | MnO. 1·37 | 14·50 | 8·01 | Na ₂ O. 4·77 | 72·66 |

L. J. S.

A Pseudo-serpentine from Stevens County, Washington. FRANK W. CLARKE (*Amer. J. Sci.*, 1903, [iv], 15, 397—398).—The material described is yellowish-green in colour, takes a fine polish, and closely resembles serpentine in appearance. Microscopical examination shows the presence of at least three minerals, and this is confirmed by the action of acids. Calculated from the following analysis

by G. Steiger, the mineralogical composition of the rock is: hydro-

magnesite, 5.0 ; chlorite, 14.0 ; serpentine, 20.0 ; brucite, 60.0 ; water, 1.0 = 100.0.

| SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | MgO. | CaO. | H ₂ O at 100°. | H ₂ O above 100°. | CO ₂ . | Total. |
|--------------------|----------------------------------|----------------------------------|------|-------|------|------------------------------|---------------------------------|-------------------|--------|
| 13.08 | 1.63 | 1.25 | 0.19 | 56.44 | 0.33 | 0.85 | 23.94 | 2.03 | 99.74 |
| L. J. S. | | | | | | | | | |

Composition of some Canadian Amphiboles. BERNARD J. HARRINGTON (*Amer. J. Sci.*, 1903, [iv], 15, 392—394).—Analysis I is of reddish-brown cleavage masses from Granville, Quebec. The presence of so much fluorine is remarkable ; another specimen contained 2.93 per cent. II is of material isolated from the essexite of Montreal ; it is black by reflected light, but brown by transmitted light. Analysis III, by N. N. Evans, is of a similar amphibole from the essexite of Mount Johnson.

| | SiO ₂ . | TiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | MnO. | CaO. | MgO. | Na ₂ O. | K ₂ O. | H ₂ O. | F. | Total. | Sp.gr. |
|----------|--------------------|--------------------|----------------------------------|----------------------------------|-------|------|-------|-------|--------------------|-------------------|-------------------|------|--------|--------|
| I. | 45.50 | 0.68 | 12.25 | 0.28 | 0.75 | 0.11 | 13.31 | 20.63 | 2.76 | 1.76 | 0.40 | 2.80 | 101.23 | 3.110 |
| II. | 39.23 | 4.53 | 14.38 | 2.92 | 8.56 | 0.65 | 11.70 | 13.01 | 3.05 | 0.98 | 0.36 | — | 99.37 | 3.159 |
| III. | 38.63 | 5.04 | 11.97 | 3.90 | 11.52 | 0.73 | 12.81 | 10.20 | 3.14 | 1.49 | 0.33 | — | 99.76 | — |
| L. J. S. | | | | | | | | | | | | | | |

Piedmontese Minerals. FERRUCCIO ZAMBONINI (*Centr. Min.*, 1903, 78—84, 117—124).—A garnet-rock from Casteldelfino consists of massive and crystallised garnet, smaragdite, and veins of calcite and diopside. On the surface are colourless, transparent crystals of grossularite with the forms {110}, {211}, &c. ; analysis gave the results under I ; crystals of a very faint yellow colour contain 0.8—1.5 per cent. Fe₂O₃. The diopside forms white, silky, crystalline masses and also prismatic crystals ; analysis II :

| | SiO ₂ . | Al ₂ O ₃ . | FeO. | CaO. | MgO. | Loss on ignition. | Total. |
|-----|--------------------|----------------------------------|-------|-------|-------|----------------------|--------|
| I. | 40.37 | 21.83 | trace | 37.06 | 0.49 | — | 99.75 |
| II. | 54.58 | 0.29 | 1.31 | 25.73 | 17.86 | 0.62 | 100.39 |

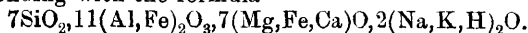
Several other minerals from various localities in Piedmont are described.

L. J. S.

A New Mineral [Grandidierite]. ALFRED LACROIX (*Compt. rend.*, 1903, 137, 582—584).—*Grandidierite* occurs in crystals 8 cm. long, with quartz, orthoclase and almandine, in the pegmatite veins at Andrahomana, Madagascar. The crystals are orthorhombic, glassy, and exhibit the phenomenon of pleochroism to a greater degree than any other known mineral, the crystals appearing colourless when viewed in the direction of their length, and bluish-green in a direction at right angles to this ; sp. gr. 2.99. Analysis, by Pisani, gave :

| SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | MgO. | CaO. | Na ₂ O. | K ₂ O. | H ₂ O. | Total. |
|--------------------|----------------------------------|----------------------------------|------|------|------|--------------------|-------------------|-------------------|--------|
| 20.90 | 52.80 | 6.60 | 4.86 | 9.65 | 2.10 | 2.22 | 0.40 | 1.25 | 100.78 |

Corresponding with the formula



M. A. W.

Spodumene from California. WALDEMAR T. SCHALLER (*Bull. Dep. Geol. Univ. California*, 1903, 3, 265—275).—Fine large crystals of transparent spodumene of gem quality have recently been found associated with lepidolite and gem tourmaline in a pegmatite vein near Pala in San Diego County. They are rose-red, magenta, or amethystine-purple in colour, rarely colourless, and exhibit well-marked etch-figures. A crystallographic description is given. The following is the average of several analyses :

| SiO ₂ . | Al ₂ O ₃ . | Mn ₂ O ₃ . | Li ₂ O. | Na ₂ O. | K ₂ O. | Total. | Sp. gr. |
|--------------------|----------------------------------|----------------------------------|--------------------|--------------------|-------------------|--------|---------|
| 64·42 | 27·32 | 0·15 | 7·20 | 0·39 | 0·03 | 99·51 | 3·189 |

L. J. S.

Presence of Heavy Metals in Sandstones. WILLIAM MACKIE (*Trans. Edin. Geol. Soc.*, 1903, 8, 256—259).—The black stains of manganese dioxide in the sandstones of the Moray Firth basin were found to contain small amounts of copper oxide (0·12 per cent.), nickel and cobalt oxides (0·69 per cent.), and lead. The sandstones themselves were also found to contain traces of these metals disseminated through them; the averages of the determinations made on several sandstones were: copper, 1 part in 77,000; nickel and cobalt, 1 part in 10,800.

L. J. S.

Chemical Composition of Ash from Mont Pelée (Martinique). ETTORE COLONNA (*Atti R. Accad. Torino*, 1903, 38, 471—476).—Volcanic ash, emitted from Mont Pelée and collected at St. Pierre, gave, on analysis :

| SiO ₂ . | TiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | MnO. | CaO. |
|--------------------|--------------------|----------------------------------|----------------------------------|-------------------|--------------------|------|
| 59·90 | 0·55 | 17·40 | 3·54 | 4·50 | slight traces | 6·70 |
| BaO. | SrO. | MgO. | Na ₂ O. | K ₂ O. | Li ₂ O. | Cl. |
| traces | traces | 2·25 | 3·35 | 0·54 | slight traces | 0·10 |
| S (as sulphide). | SO ₃ . | P ₂ O ₅ . | Loss on heating. | Total. | | |
| 0·31 | 0·48 | 0·11 | 0·50 | 100·23 | | |

These numbers are compared with those obtained by Pisani (*Compt. rend.*, 1902, 134, 1328), Schmelck (*Abstr.*, 1903, ii, 224), and Hillebrand (*J. Amer. Chem. Soc.*, 1902, 24, 362).

T. H. P.

Meteoric Iron from N'Goureyima, Soudan. EMIL W. COHEN (*Amer. J. Sci.*, 1903, [iv], 15, 254—258).—This iron, which weighed 37½ kilos., fell on June 15, 1900, at N'Goureyima, near Djenne, Province of Macina, Soudan. The structure is coarsely granular; sp. gr. 7·672. A remarkable feature is presented by the presence of enormous numbers of small bars of troilite of regular and uniform distribution. The peculiarities in form and structure of the mass suggest

Physiological Chemistry.

Respiratory Capacity of Certain Invertebrates. CHARLES DHÉRE (*Compt. rend. Soc. Biol.*, 1903, 55, 1161—1162).—A few analytical figures are given of the amount of oxygen and of copper in the blood of certain animals which contains hæmocyanin (octopus, crab, &c.). Hæmocyanin resists putrefaction to some extent. When putrefaction occurs in the blood, the oxyhæmocyanin is reduced, but the blue colour returns on shaking with air. W. D. H.

Effect of Rarefied Air on Blood Pressure. FREDERIC H. BARTLETT (*Amer. J. Physiol.*, 1903, 10, 149—163).—Experiments on rabbits show that rarefaction in the air causes dyspnœa, and in some cases asphyxia. The arterial blood pressure falls. Cutting the vagi intensifies the effects. The conclusion is drawn that in mountain sickness there is an increased amount of blood in the pulmonary vessels, due to an increase in their capacity, and to a stagnation of blood arising from an equalisation of the atmospheric and intra-thoracic pressures. Work aggravates the symptoms. W. D. H.

Caisson Disease and Diver's Palsy. LEONARD ERSKINE HILL and JOHN J. R. MACLEOD (*J. Hygiene*, 1903, 3, 401—445).—Examination, *ante*- and *post-mortem*, of numerous cases of illness due to the patients having worked in caissons, or as divers, and experiments on animals in addition, show that the symptoms are always the result of decompression, and the consequent liberation of gas in the blood.

W. D. H.

Analysis of the Air of the House of Commons. W. J. ATKINSON BUTTERFIELD (*J. Hygiene*, 1903, 3, 486—497). **Micro-organisms in the same Air.** G. S. GRAHAM-SMITH (*ibid.*, 498—513).—The general conclusion reached is that the air supply to the House of Commons is exceptionally good, being adequate to avoid a rise of two volumes of carbon dioxide over that present in the incoming air, except close to the ceiling, where the rise is somewhat greater. This is much better than most authoritative standards.

The number of micro-organisms in the open space surrounding the buildings is comparatively small (4.2 per litre on the ground level, and 1.4 at the top of the tower); the air in the debating chamber during a sitting is remarkably pure from the bacteriological stand-

point (5·8 per litre, mean of 11 experiments). In the committee, dining, and smoking rooms, the number is larger (32·3 per litre, mean of 6 experiments). No organisms associated with specific diseases in man, and only a few pathogenic to animals, were isolated.

W. D. H.

Activity of Nerves on the Heart Perfused with Ringer's Solution. H. E. HERING (*Pflüger's Archiv*, 1903, 99, 245—252). **Action of the Salts of Ringer's Solution on the Isolated Mammalian Heart.** EMANUEL GROSS (*ibid.*, 264—322).—The experiments were performed in a dead animal by perfusing the heart with Ringer's solution, and with a simplified circulation consisting of the pulmonary circuit, and the coronary vessels. In a monkey, vagus action could be demonstrated in 6 hours, and the action of the accelerator nerves nearly 54 hours later. The conclusion is drawn that the accelerator does not act through the intermediation of ganglion cells on the heart. The second paper relates to the action of the individual salts of Ringer's solution on the isolated surviving heart of mammals, and results were obtained comparable to those published many years ago by Ringer in connection with the frog's heart, results which Loeb has shown are to be interpreted as due to the action of ions.

W. D. H.

Blood of the New Born. ALEX. O. M. FEHRSEN (*J. Physiol.*, 1903, 30, 322—329).—An examination of the blood in forty new born infants shows a high percentage of hæmoglobin (10 to 15 per cent. over the normal); a large increase of red corpuscles with a mean of over six millions per c.mm.; a well-marked leucocytosis (18,000 per c.mm.); an absolute and relative increase in the lymphocytes and large mononuclear cells; the invariable presence of nucleated red corpuscles up to the third hour after birth, and a high colour index.

W. D. H.

Blood of the Skate. DAVID FRASER HARRIS (*J. Physiol.*, 1903, 30, 319—321).—Even in large skates (weighing 600 to 900 grams) there are only about 15 to 20 c.c. of blood; for analytical purposes, a sufficient supply can be obtained from the heart. The blood clots in 5 to 6 minutes. The percentage of hæmoglobin is from 20 to 30 per cent. in Orion's scale, which corresponds with a percentage of 3·5 to 3·8 in the blood. The blood has a sp. gr. 1·035 to 1·038. The number of red corpuscles per c.mm. is 350,000, but this seems to vary with the season. The amount of hæmoglobin per corpuscle is $3\frac{1}{4}$ times as great as in man. The number of leucocytes in the same volume of blood varies from 20,000 to 30,000. The red to white ratio is therefore 10 or 12 to 1.

W. D. H.

Hydroxyl Ions of the Blood. II. RUDOLF HÖBER (*Pflüger's Archiv*, 1903, 99, 572—593. Compare Abstr., 1901, ii, 738).—If platinum electrodes are placed in a mixture of hydrogen and carbon dioxide, they behave like hydrogen electrodes under diminished pressure; the carbon dioxide is electrically indifferent. If the *E.M.F.* of such a chain as $H_2 + CO_2 \mid HCl \mid$ defibrinated blood $\mid H_2 + CO_2$ is

investigated, and the concentration of hydroxyl ions in the blood calculated for different tensions of carbon dioxide, it is found that at 0 pressure, the hydroxyl equals $40 \cdot 10^{-7}$, at 0.6 atmosphere pressure, $0.2-10^{-7}$, and at the physiological pressure of 0.028 to 0.054 atmosphere, 2 to $0.7-10^{-7}$ gram ions. The amount of hydroxyl ions in defibrinated and also in unclotted blood at the CO_2 tension of arterial blood is twice as great as at the CO_2 tension of venous blood. Blood contains somewhat more hydroxyl ions than serum at the same CO_2 tension; the difference is greater when this tension is higher. This is due to interaction of HCO_3 and Cl between corpuscles and serums.

W. D. H.

Behaviour of Carbon Monoxide in the Organism. I. PIERO GIACOSA (*Atti R. Accad. Torino*, 1902—1903, 38, 864—882).—A number of experiments were made with the object of deciding the much-discussed question of the oxidisability of carbon monoxide in the blood. The preliminary experiments showed that blood, either obtained from an animal poisoned with carbon monoxide or saturated with the gas after extraction from a healthy animal, and then defibrinated and introduced into tubes kept at 38° , continues to emit carbon monoxide for some hours, at first rapidly, but afterwards with less activity. It is further found that, in presence of fresh pulmonary tissue, part of the carbon monoxide in such blood is oxidised and the decomposition of the carbon monoxide-hæmoglobin compound is accelerated.

T. H. P.

Does Glycerol exist in Normal Blood? ANTOINE MOUNEYRAT (*Compt. rend. Soc. Biol.*, 1903, 55, 1207—1208. Compare Nicloux, *Abstr.*, 1903, ii, 337, 438, 560).—A criticism of Nicloux's methods.

W. D. H.

Glycerol in the Blood. MAURICE NICLOUX (*Compt. rend. Soc. Biol.*, 1903, 55, 1229—1231. Compare *Abstr.*, 1903, ii, 438).—A reply to Mouneyrat (preceding abstract).

W. D. H.

Sugar in the Blood. RAPHAEL LÉPINE and BOULUD (*Compt. rend.*, 1903, 137, 686—689. Compare *Abstr.*, 1901, ii, 610; 1902, ii, 218, 434).—In some cases, fresh venous blood contains more sugar than arterial blood. In the same specimens, an hour later, the sugar in the arterial blood rises above that in the venous blood, which remains stationary. The explanation offered is that free sugar is formed or liberated from some other compound (*sucre virtuel*).

W. D. H.

Albumoses in the Blood. O. SCHUMM (*Beitr. chem. Physiol. Path.*, 1903, 4, 453—459).—In a case of nephritis, proteoses were found in the blood; traces were also observed in a case of pernicious anæmia, but none in healthy human blood.

W. D. H.

The Fertilisation of the Eggs of Echinoderms. JACQUES LOEB (*Pflüger's Archiv*, 1903, 99, 323—356; 637—638. Compare *Abstr.*, 1902, ii, 151).—The eggs of *Strongylocentrotus purpuratus* can be

easily fertilised with the sperm of the same species, either in sea-water or van't Hoff's saline solution, which contains the salts of sea-water in the proper proportion, if there is added to 100 c.c. of the solution from 0.1 to 0.2 c.c. of a decinormal solution of sodium hydroxide. Under the same circumstances, they cannot be fertilised, or only slightly, by the sperm of the star-fish, *Asterias ochracea*, but fertilisation occurs if 0.3 to 0.4 c.c. of decinormal sodium hydroxide is added to 100 c.c. of van't Hoff's solution. Using this high proportion of alkali, the eggs are no longer fertilisable by sperm of the same species.

Further experiments confirm the hypothesis that the addition of alkali is necessary to neutralise acid substances produced in the egg, and that it is improbable that in normal fertilisation free hydroxyl ions are necessary.

W. D. H.

Proteolytic Action of Extracts of Intestine and Pancreas. ERNST WEINLAND (*Zeit. Biol.*, 1903, 45, 292—297).—Experiments were made on fibrin and Witte's peptone, subjected to the action of pancreatic extracts and extracts of the intestine. In both cases, in time, products appeared which no longer gave the biuret reaction. The time occupied was slower than that described by Cohnheim in his work on erepsin. Alkalinity increases the time. In all such experiments, besides reaction, the presence of antiferments, and Vernon's hypothesis that several trypsin exist must be taken into account.

W. D. H.

The Peptone-splitting Ferments of the Pancreas and Intestine. HORACE M. VERNON (*J. Physiol.*, 1903, 30, 330—369).—The peptone-splitting power of ferments can be estimated colorimetrically by the biuret test. The full colour takes some minutes to develop. The time required to split up peptone varies inversely as the quantity of the ferment. In pancreatic extracts, the power is due mainly to pancreatic erepsin, which is quite distinct from trypsin. Such extracts contain but little trypsin (only trypsinogen), and have little or no action on fibrin. When free trypsin appears, the peptone-splitting power is less, probably because trypsin destroys erepsin. Neither pancreatic or intestinal erepsin exists in a soluble zymogen form. Pancreatic erepsin is more readily precipitable by alcohol than intestinal erepsin, and differences in the activity of the two ferments are also noted. The action of both is accelerated by increasing alkalinity up to 0.4 to 1.2 per cent. of sodium carbonate.

W. D. H.

Action of Alkaline Soaps on the Pancreatic Secretion. C. FLEIG (*Compt. rend. Soc. Biol.*, 1903, 55, 1201—1202. Compare Abstr., 1903, ii, 385).—The stimulating action of alkaline soaps on pancreatic secretion is not due to a nervous reflex, but is "humoral" in its action. It produces in the intestine a substance analogous to Bayliss and Starling's secretin.

W. D. H.

Proteolytic Enzymes of Ox-spleen and Serum. SVEN G. HEDIN (*J. Physiol.*, 1903, 30, 155—175, 195—201. Compare Abstr., 1901, ii, 402).—Ox-spleen contains two proteolytic enzymes α -*protease*, acting in an alkaline, and β -*protease* in an acid, medium. When obtained in combination with nuclein, they are insoluble in weak acetic acid; when freed from nuclein, they are soluble in this acid. The serum contains anti-substances for the α -, but not for the β -variety. Their action is probably intracellular in the main.

Ox-serum contains a weak proteolytic ferment, which acts in an alkaline medium; this is precipitable with the globulin fraction of the proteids. It is destroyed by heating at 55° for half an hour. It acts on casein, gelatin, and coagulated serum, but not on the globulin itself or on coagulated albumin. Anti-substances, mainly contained in the albumin fraction, prevent it from acting in the serum.

W. D. H.

Influence of Hydrochloric Acid introduced into the Intestine on the Secretion of Bile. ARTHUR FALLOISE (*Bull. Acad. Roy. Belg.*, 1903, 757—791).—Hydrochloric acid introduced into the intestine acts as a cholagogue, but this action is manifested only by its action on the duodenum, and first part of the jejunum. Its action is not immediate, but is preceded by a latent period of from three to five minutes. The flow follows a course similar to that of the pancreatic juice, reaching a maximum from the seventh to the twelfth minute after the injection, and then progressively diminishing until about the twenty-fifth minute. The amount excreted may be four times the volume formed previous to the injection. This is not influenced by anæsthesia or by large doses of atropine. The mechanism is doubtless chemical, like that of prosecretin and secretin in the case of the pancreas.

W. D. H.

Influence of Pituitary Gland Substance on Metabolism. JOHN MALCOLM (*J. Physiol.*, 1903, 30, 270—280).—Pituitary bodies from oxen were added to the diet of dogs, and metabolism experiments made in the usual way. The glandular lobe of the pituitary in a dry form tends to cause a retention of nitrogen and probably of chlorine, whilst the output of phosphorus and calcium is increased. There is no diuretic action, as when extracts are given intravenously. Fresh gland substance has the opposite effect on the nitrogen and calcium. The nervous portion of the gland is probably more active than the glandular, and the effect lasts longer.

W. D. H.

Chauveau's Researches on [the Nutritive Value of] Alcohol. RUDOLF ROSEMAN (*Pflüger's Archiv*, 1903, 99, 630—633. Compare Abstr., 1901, ii, 668).—Polemical against Kassowitz.

W. D. H.

Time Relations of Proteid Metabolism. PHILIP B. HAWK (*Amer. J. Physiol.*, 1903, 10, 115—145).—The experiments were made on two subjects; in both, the normal curve of nitrogen excretion showed two maxima. On a day of extra proteid ingestion, a single

maximum occurred. After this ingestion, the curve rose rapidly and immediately, reaching the maximum in six to nine hours in one, and in nine to twelve hours in the other subject; after this, the curve fell rapidly. The course of sulphur excretion was in general terms like that of nitrogen. The minimum phosphorus excretion occurred in the morning after breakfast. W. D. H.

Comparative Physiology of Inanition. II. Inanition in the Snail. B. SLOWTZOFF (*Beitr. chem. Physiol. Path.*, 1903, 4, 460—475).—In inanition, the snail loses 25·74 per cent. of its weight and 28·4 per cent. of its total energy. The daily loss is regular, and there is no *pre-mortem* increase. The shell shares in the wasting, losing 25·5 per cent. of its weight; both organic and inorganic constituents of the shell remain in the same proportion throughout. Full details are given in regard to each constituent of the body. W. D. H.

Osmotic Regulation of Fluids in the Interior of Echinoderms. VICTOR HENRI and S. LALOU (*Compt. rend.*, 1903, 137, 721—723).—The membranes that separate the fluid in the interior of sea-urchins from the external fluid are semipermeable. The same is true for the respiratory membrane and the digestive tube in Holothurians. They allow water to pass but not chlorides, sulphates, urea, or sugar. In this, these membranes resemble that composing the stomach of *Aphysia* described by Botazzi and Enriques. W. D. H.

Local Retention of Chlorides following Injection of Different Substances. CH. ACHARD and L. GAILLARD (*Compt. rend. Soc. Biol.*, 1903, 55, 1189—1190).—If various indifferent crystallised substances (urea, creatine, dextrose) are injected into the tissues or into the serous cavities, there is gradual absorption of these substances and at the same time a transudation of sodium chloride which remains for a time after the absorption of the foreign material. If this retention is excessive, it may lead to hypochloruria. W. D. H.

Origin of Organic Chlorine Compounds. J. PERIN (*Compt. rend. Soc. Biol.*, 1903, 55, 1166—1167).—Chlorine occurs in the intestine in three forms, hydrochloric acid, sodium chloride, and organic chlorine compounds. The last are stated to exist in the substance of the intestinal mucous membrane of the dog, but not in the intestinal juice. These substances are believed to originate in the stomach, to pass thence to the intestine, where they are absorbed, and taken to the liver by the portal blood. They are stated to be discoverable in the portal blood and in the liver. W. D. H.

The Precursors of Fibrin Ferment. P. MORAWITZ (*Beitr. chem. Physiol. Path.*, 1903, 4, 381—420).—Thrombin or fibrin ferment is described as consisting of two substances named α - and β -thrombin respectively; each is preceded by a precursor, α - and β -prothrombin. α -Prothrombin is the prothrombin of Arthus and Pekelharing, which is converted into α -thrombin by calcium salts. β -Prothrombin is con-

verted into β -thrombin by certain substances termed "zymoplastic," such as alkalis, acids, and alcohol, but not by calcium salts. The presence of antithrombin in the blood is probable. Such a hypothesis is stated to explain previous divergences of views. Fresh serum contains α -thrombin and β -prothrombin; old serum only the latter; Schmidt's fibrin ferment contains both thrombins; oxalate plasma, only α -prothrombin; and fluoride plasma neither thrombin nor its zymogens.

W. D. H.

[Amount] of Urea in the Tissues and Blood of Vertebrate Animals. NESTOR GREHANT (*Compt. rend.*, 1903, 137, 558—560. Compare Abstr., 1889, 914).—The author records the following percentages of urea: muscle of rabbit, 0.042; guinea-pig, 0.045; duck, 0.000; frog, 0.044; carp, 0.021; ray, 1.37; blood of rabbit, 0.043; guinea-pig, 0.045; duck, 0.000 (compare Garrod, Abstr., 1893, ii, 581; Schondorff, Abstr., 1899, ii, 374). Experiments on the torpedo of Arcachon indicate that the quantity of urea in the electric organ is considerably increased by artificial excitation.

M. A. W.

Physiology of Muscle in Warm Blooded Animals. WALTHER FREUND (*Beitr. chem. Physiol. Path.*, 1903, 4, 438—441).—In warm blooded animals, the muscles are isotonic with a 1.1 to 1.5 per cent. solution of sodium chloride. This is higher than in the frog where the number is 0.7 (Loeb).

W. D. H.

Hæmoglobin in Muscles. KARL B. LEHMANN, ARMIN WERNER, HEINRICH STADTFELD, SAMUEL MANDELBAUM, ISIDOR EISENLAUER, and ALBERT IMHOF (*Zeit. Biol.*, 1903, 45, 324—345).—The result of a large number of observations on the amount of hæmoglobin obtained from various muscles of different animals is given. The muscles were obtained as fresh as possible and therefore contained blood. Speaking generally, the amount of blood pigment is proportional to the activity of the muscles; thus it increases as the muscles become active after birth; in the heart, this increase with age is least noticeable. The heart and diaphragm yield most pigment. The muscles of cold-blooded animals are not deeply coloured; this is related to their low metabolism. Smooth muscles yield but little hæmoglobin.

W. D. H.

Glycolytic Action of the Liver. RAHEL HIRSCH (*Beitr. chem. Physiol. Path.*, 1903, 4, 535—542).—The glycolysis which occurs in the liver during self digestion is also manifested on dextrose added to the minced organ. The acids formed during autolysis (lactic, succinic, butyric, &c.) are probably derived from the sugar. The addition of pancreas to the mixture greatly increases the rate and amount of loss of the sugar; whether this is of physiological importance in the relationships of the two organs has still to be determined.

W. D. H.

The Pancreas and Glycosuria. JEAN LÉPINE (*Compt. rend. Soc. Biol.*, 1903, 55, 1288—1289).—Injection of sugar in guinea-pigs pro-

duces no change in the islets of Langerhans of the pancreas as Soboleff has stated. Prolonged glycosuria, such as that caused by phloridzin, leads to a slight overgrowth of the islets. Perhaps this indicates a defensive action against glycosuric conditions of extra-pancreatic origin.

W. D. H.

The Sugar-destroying Ferment in Organs. J. FEINSCHMIDT (*Beitr. chem. Physiol. Path.*, 1903, 4, 511—534).—Glycolysis is a cellular function, and occurs in the minced pancreas, liver and muscles, and also in the juices expressed from them. It is evidently a ferment action, and the ferment was to some extent isolated. Among the products of glycolysis are abundant quantities of carbon dioxide, a small amount of alcohol, and acid substances in large amount. The diabetic liver has no glycolytic power.

W. D. H.

Osseo-mucoid. CHRISTIAN SIEFERT and WILLIAM J. GIES (*Amer. J. Physiol.*, 1903, 10, 146—148).—Osseo-mucoid was found in the bones of twenty animals of different genera. It is therefore a probable constituent of all bones.

W. D. H.

Conference of Passive Immunity on the same Species, and on a Species other than that providing the Antitoxic Serum. ERNEST F. BASHFORD (*J. Pathol. Bacteriol.*, 1903, 9, 192—201).—The antitoxin of one species is not quite passive in another species, but evolves a reaction. The existence of anti-antitoxin is regarded as the cause of this.

W. D. H.

Leucocytes and Bacteriolysis. GEORGE F. PETRIE (*J. Pathol. Bacteriol.*, 1903, 9, 130—153).—Although there is a possibility of the leucocytes acting as secretors of alexin or complement, the cytases are not preformed within the cells; the experiments recorded show that no bactericidal substances for the bacteria selected can be obtained from any variety of leucocyte, nor from the cells of spleen, liver, or bone-marrow.

W. D. H.

Destruction of Adrenalin in the Organism. GUSTAV EMBDEN and OTTO VON FÜRTH (*Beitr. chem. Physiol. Path.*, 1903, 4, 421—429).—Suprarenin (adrenalin) is capable of passing unchanged through the vessel's walls, but most of it is destroyed in the blood, probably by oxidation. No particular organ or tissue is proved to have any destructive influence on this substance, although possibly the liver is concerned in the process.

W. D. H.

Influence of Irritants on Milk Secretion. GUSTAV FINGERLING (*J. Landw.*, 1903, 51, 287—288).—Malt germs (added to a food consisting of straw, starch, and oil) affected the quality but not the yield of milk. Fenugreek had no effect, whilst hay-distillate and fenchel increased the yield. In every case (except with fenugreek), the milk fat was increased.

When the animals (sheep and goats) were fed with hay, the addition of these substances had no effect.

N. H. J. M.

Minimal Intake and Excretion of Potassium in the Urine. E. MAUREL (*Compt. rend. Soc. Biol.*, 1903, 55, 1282—1284. Compare Abstr., 1901, ii, 565).—In the adult on maintenance diet, 0.06 gram of potassium per kilo. of body-weight is sufficient. 0.07 is sufficient during growth, and in the adult during convalescence from disease.

W. D. H.

The Minimal Excretion of Nitrogen. E. MAUREL (*Compt. rend. Soc. Biol.*, 1903, 55, 1279—1281).—The experiments made on the author's person with insufficient nutriment confirm those of Burt, Bouchard, and von Noorden. However small the quantity of nitrogen taken in, the excretion never falls below from 0.08 to 0.09 gram per kilo. of body-weight.

W. D. H.

Influence of Diet, Muscular Exertion, and Loss of Sleep on the Formation of Uric Acid in Man. HENRY C. SHERMAN (*J. Amer. Chem. Soc.*, 1903, 25, 1159—1166).—Both with professional athletes and with the subject of sedentary habits, the elimination of uric acid is primarily dependent on the food consumed. Whilst very small changes resulted from large variations in the amount of a bread-and-milk diet, the elimination of uric acid was mainly determined by the quantities of meat products consumed. Prolonged muscular exertion in well-trained athletes had little influence on the formation and elimination of uric acid. Marked loss of sleep had no apparent influence on the amount of uric acid eliminated.

A. McK.

Relation between Uric Acid Excretion and White Corpuscles. O. K. WILLIAMSON (*Trans. Path. Soc. London*, 1903, 54, 265—285).—A number of cases of disease are described in which, on the whole, there is a parallelism between the excretion of uric acid (and in some cases of phosphoric acid also) and the amount of breaking down of the colourless corpuscles of the blood.

W. D. H.

Absence of Neutral Sulphur in Normal Urine. L. MONFET (*Compt. rend. Soc. Biol.*, 1903, 55, 1169—1171).—The so-called neutral sulphur of urine is only sulphuric acid united to the phenol group, which is stable in the presence of hydrochloric acid. A litre of urine contains about a gram of ethereal sulphates; of this total, the indole-scatole group accounts for one-third, and the phenol-cresol group for the remainder. Potassium indoxyl sulphate is a normal constituent of urine; whereas indican is abnormal, and is spoken of as a gluco-derivative.

W. D. H.

Lipolytic Power of Icteric Urine. CHARLES GARNIER (*Compt. rend. Soc. Biol.*, 1903, 55, 1180—1181).—Icteric urine containing bile pigments hydrolyses monobutyryl, but normal urine does not. This action is not destroyed by boiling, but is due to the presence of certain biliary constituents. Bile has the same power, which is also not lost after boiling. The bile salts do not possess the property, but possibly the bile pigments are the substances to which it is due.

W. D. H.

Urinary Indican. L. MONFET (*Compt. rend. Soc. Biol.*, 1903, 55, 1211—1213).—Urinary indican is a gluco-compound. It appears in the urine when the combination with sulphuric acid is insufficient. Its formation is an additional act of defence against indole poisoning.
W. D. H.

Urinary Indoxyl. C. HERVIEUX (*Compt. rend. Soc. Biol.* 1903, 55, 1294—1295).—A criticism of Monfet's method of estimating indican, and a restatement of the author's view of the two ways in which indoxyl occurs in the urine, namely, as a sulpho- and as a gluco-compound.
W. D. H.

Ehrlich's Diazo-reaction in Urine. L. MONFET (*Compt. rend. Soc. Biol.* 1903, 55, 1275—1277).—Whenever this reaction is positive in urine, that fluid contains excess of conjugated derivatives of indole and scatole which indicates excess of putrefactive processes.
W. D. H.

Action of Saline Purgatives. JOHN BRUCE MACCALLUM (*Amer. J. Physiol.*, 1903, 10, 101—110).—A fuller account of observations already published (*Abstr.*, 1903, ii, 742).
W. D. H.

Behaviour of Human Semen towards Solutions of Mercuric Chloride. NAZARENO TARUGI (*Chem. Centr.*, 1903, ii, 1077—1078; from *Boll. Chim. Farm.*, 42, 577—579).—When a 1 per cent. solution of mercuric chloride is added to human semen, a white, flocculent precipitate is formed, which settles after a time and leaves a perfectly clear supernatant liquid. The whole of the spermine is contained in this precipitate, together with other substances which do not interfere, however, with the spermine phosphate test. When ammonium phosphate is added to a solution of the precipitate in ammonia of sp. gr. 0.96, spermine phosphate is precipitated; a solution of the precipitate in a 35 per cent. solution of acetic acid gives the biuret reaction, and also forms precipitates with phosphomolybdic acid, phosphotungstic acid, a saturated solution of sodium chloride, and a solution of iodine in potassium iodide
E. W. W.

Cerebrospinal Fluid. ISADOR H. CORIAT (*Amer. J. Physiol.*, 1903, 10, 111—114).—An analysis of the fluid from a case of hydrocephalus. The freezing point was -0.65° , and the relation $\Delta : \text{NaCl} = 0.97$. The total proteid was 1.18 gram per litre, and consisted of globulin. Catechol and choline were absent; sugar was present.
W. D. H.

Production of Choline in the Cerebrospinal Fluid in Cases of Epilepsy and Nervous Diseases. JULIUS DONATH (*Zeit. physiol. Chem.*, 1903, 39, 526—544. Compare Mott and Halliburton, *Abstr.*, 1901, ii, 260, 463; Zdarek, *Abstr.*, 1902, ii, 528).—Choline has been detected in the cerebrospinal fluid taken from epileptic patients, and this is regarded as the actual poison causing the fits.

It is found that by intracerebral application of choline or of neurine, severe paralytic effects are produced.

Other substances found in the cerebrospinal fluid are sodium chloride, potassium and ammonium salts, and phosphates. In two cases, no ammonia was found, and in two other instances lecithin was observed. A substance with reducing properties, probably dextrose, is also present. Choline cannot be detected in the urine of animals to whom it has been administered either intracerebrally or intravenously. It appears to be readily oxidised.

The choline was always isolated in the form of its platinichloride. For this purpose, the liquid is evaporated to dryness on the water-bath and then extracted with 100 per cent. alcohol, when the alkali chlorides remain undissolved and only choline hydrochloride goes into solution. The platinichloride is obtained by the addition of an alcoholic solution of platinic chloride to the solution. It is characterised by being readily soluble in water and by its crystallographic form.

J. J. S.

Cholesteatoma of the Brain. H. MORLEY FLETCHER (*Trans. Path. Soc. London*, 1903, 54, 308—310).—A case of this rare form of brain tumour is described. The cholesterol appears to originate from the breakdown of cells, but the endothelial origin of the cells is doubtful.

W. D. H.

Proteolytic Ferment in the Blood in Myelogenic Leucæmia. O. SCHUMM (*Beitr. chem. Physiol. Path.*, 1903, 4, 442—452. Compare Abstr., 1903, ii, 731).—The presence of proteoses, peptone (in Kühne's sense), leucine and tyrosine is described in the blood of two cases of this disease; this is attributed to the presence of a proteolytic ferment in that fluid. Further investigation of the bone marrow in such cases is necessary.

W. D. H.

Multiple Myeloma and Albumosuria. F. PARKES WEBER (*J. Pathol. Bacteriol.*, 1903, 9, 172—191).—Details of a case of bone disease are given, in which the albumose called Bence-Jones' albumin occurred in the urine. References and short details are also given of 39 hitherto recorded cases of the same condition.

W. D. H.

Albumoses in Tubercular Sputum. OSCAR SIMON (*Chem. Centr.*, 1903, ii, 897; from *Arch. exp. Path. Pharm.*, 49, 449—456).—Kühne showed that Koch's tuberculin contained a mixture of albumoses precipitable by acetic acid. This acro-albumose is regarded as identical with the proteid found in exudations by Umber and Stähelin. It is, however, not found in tubercular sputum. The albumoses present are different; they arise as the result of microbic and autolytic processes. A method of isolating them is described; the alcoholic filtrate is stated to contain a peptone-like substance. They give the ordinary proteid tests, and contain loosely-bound sulphur. Injected into healthy animals, they cause rise of body temperature, whilst in tuberculous animals they produce high fever.

W. D. H.

Lime Deposits in the Kidneys. EDWIN BEER (*J. Pathol. Bacteriol.*, 1903, 9, 225—233).—Calcareous deposits in the kidneys, especially after the age of 24, are very common, even when no bone disease exists. The majority cannot be classed as metastatic, and are accompanied with chronic interstitial nephritis. W. D. H.

Proteids of the Body during Inanition. FERDINAND BLUMENTHAL (*Chem. Centr.*, 1903, ii, 842; from *Deutsch. med. Woch.*, 29, 437—439).—During inanition and in phloridzin diabetes, the blood proteid loses its carbohydrate group. A contrast is drawn between this and the nucleins, which are regarded as of little use in nutrition, but they favour oxidation processes; they contain iron and phosphorus, and are important for the vital functions. The purine bases they contain are excreted, but the pentose group is incompletely used. W. D. H.

Action of Lead, Mercury, Phosphorus, Iron, and Quinine on the Bone-marrow of Rabbits. RALPH STOCKMAN and FRANCIS J. CHARTERIS (*J. Pathol. Bacteriol.*, 1903, 9, 202—208).—Chronic lead poisoning causes marked anæmia; the bone-marrow, after increased activity, shows gelatinous degeneration and complete atrophy. The results with mercury are very similar, but the degeneration occurs very early. Phosphorus produces the same result, and also fatty degeneration in other tissues. Iron has no such effect, but promotes the formation of new blood corpuscles. Quinine has no effect on the marrow. W. D. H.

Action of Various Monohydric Alcohols on Ciliated Epithelium and Motor Nerve Fibres. HANS BREYER (*Pflüger's Archiv*, 1903, 99, 481—512).—The main effect of alcohols on these structures is first depression, then stimulation, and finally depression again. The depression increases with the concentration of the alcohol, and with its molecular weight. Cilia continue working much longer in a decinormal solution of alcohol than in saline solution. Extensive references to the whole alcohol question are given. W. D. H.

Action of Choline, Neurine, Muscarine, and Betaine on Isolated Nerve and Heart. AUGUSTUS D. WALLER and S. C. M. SOWTON (*Proc. Roy. Soc.*, 1903, 72, 320—345).—The toxicity of these ptomaines decreases in the following order: neurine, muscarine, choline, and betaine. The effect on nerve is to lessen or abolish the action current: the effect on the heart is diastolic arrest; this is counteracted by atropine. W. D. H.

Physiological Action of Betaine extracted from Raw Beet-sugar. AUGUSTUS D. WALLER and R. H. ADERS PLIMMER (*Proc. Roy. Soc.*, 1903, 72, 345—352).—Betaine is present in raw beet-sugar in considerable quantities (3·75 per 1000). In view of the work of Waller and Sowton (see preceding abstract), it can no longer be considered an inert substance. W. D. H.

Toxicity of Benzene and its Homologues. ALLYRE CHASSEVANT and M. GARNIER (*Compt. rend. Soc. Biol.*, 1903, 55, 1255—1257).—The toxicity on guinea-pigs of various aromatic hydrocarbons is given in tabular form. The action depends on the molecular weight, the number of substitutions, and the position of the substituted radicles. Mono-substitution products are the most toxic.

W. D. H.

Strychnine and Persodine. G. BUFALINI (*L'Orosi*, 1902, 25, 332—337).—Persodine, which is a special preparation composed of a mixture of the persulphates of sodium and ammonium, acts as an antidote in cases of strychnine poisoning. The strychnine is converted by this reagent into either oxystrychnine or strychnol, which are both products of much less toxicity than strychnine itself. The author gives details of a number of experiments on the effect of persodine on rabbits to which strychnine had been administered.

T. H. P.

Physiological Action of Apocodeine. WALTER E. DIXON (*J. Physiol.*, 1903, 30, 97—131).—Apocodeine paralyses nerve cells like nicotine, but without any initial stimulation. After the paralysis produced by apocodeine, nicotine is without effect, but adrenalin still acts typically. In a series of four opium alkaloids, the purgative action varies directly with their paralytic effect on sympathetic ganglia. Larger amounts of apocodeine act like curare on the voluntary muscles, and like atropine on the heart. With still larger doses, paralysis of vaso-motor nerve endings is produced; under these circumstances, pilocarpin, physostigmin, and adrenalin have no effect on blood vessels, whilst barium salts and digitalis still constrict them; the former three drugs, therefore, act on nerve endings, and the latter two on muscular fibres. The accelerator nerves of the heart are paralysed; caffeine and aconitine, however, subsequently quicken the heart, and so act on muscle. Both motor and inhibitory nerves of the intestines are paralysed, but the terminals of the hypogastrics are not affected.

W. D. H.

Physiological Action of Atropine and the Hyoscyamines. ARTHUR R. CUSHNY (*J. Physiol.*, 1903, 30, 176—194).—A full description of experiments of which a preliminary account has already appeared.

W. D. H.

Action of Extracts of Nervous Tissues and Blood. SWALE VINCENT and WILHELM CRAMER (*J. Physiol.*, 1903, 30, 143—154).—A full description of experiments of which a preliminary account has already appeared (*Abstr.*, 1903, ii, 673).

W. D. H.

Action of Tissue Extracts on Protoplasm. J. W. SCOTT-MACFIE (*J. Physiol.*, 1903, 30, 264—269).—Extracts of suprarenal, pituitary thymus, brain, testis, and other organs have no action on protoplasmic structures when applied directly to them. Some rather alter the rate of ciliary movement, but there is no specific action; the activity of leucocytes is not altered at all; neither is the beat of the embryonic heart.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Thermophile Bacteria from various Foods and Milk and the Products formed when these Bacteria are Cultivated in Media containing Carbohydrates. FRANZ SCHARDINGER (*Zeit. Nahr. Genusssm.*, 1903, 6, 865—880).—Experiments were carried out with two groups of bacteria, one group being cultivated at temperatures varying from 15° to 55°, and the other from 37° to 66°. The species belonging to group I, when grown upon media containing starch-paste, formed a crystallisable dextrin, $C_6H_{10}O_5 \cdot 3H_2O$ (compare Abstr., 1891, 659), together with acetic and *l*-lactic acids. The anaerobic bacteria belonging to this group produced a small quantity of butyric acid. The bacteria included in Group II were obtained from milk which had been kept at a temperature of 60° for 24 hours. With starch-paste, these bacteria formed acetic, butyric, and *l*-lactic acids. The butyric acid was only present in small quantity. Fermentation experiments with the anaerobic bacteria showed that no alcohol was produced, although there was a considerable evolution of gas. In this case, butyric and inactive lactic acids were formed. W. P. S.

Reduction of Sulphates by Bacteria. A. VAN DELDEN (*Centr. Bakt. Par.*, 1903, ii, 11, 81—94).—The optimum temperature for *Microspira desulfuricans* is between 25° and 30°, but even at 37° hydrogen sulphide is produced abundantly. The organic matters usually present in polluted waters are suitable for the reducing organism. Lactates, malates, and succinates are the most suitable organic salts, whilst nitrogen is assimilated in the form of asparagine, peptone, and ammonium salts. Nitrates hinder the reduction. Sulphate reduction takes place in canal and river water after a little potassium phosphate, sodium lactate, and asparagine have been added; it is suggested that the reduction might be utilised, in conjunction with an iodometric titration, for estimating the amount of sulphate present in water.

Cultivations in gelatin containing hydrogen sulphide produced sulphur at the surface to a depth of about 1.5 cm.

A bacterium was isolated which does not reduce sulphates, but reduces sulphites and thiosulphates, and, with limited access of oxygen, oxidises the hydrogen sulphide to sulphur. The bacterium resembles *Microspira desulfuricans* and differs from *Bacterium hydrosulfureum pontican* in not growing in air.

Experiments with sea water, to which mineral and organic substances were added, showed that reduction of sulphates sometimes occurred, but not always. Inoculation with sea sand and addition of sodium sulphite generally resulted in reduction, whilst inoculation with mud obtained at low tide at a depth of 10 cm. invariably induced reduction. Sea water can be entirely freed from sulphates when sufficient organic matter is added.

N. H. J. M.

Reduction of Sulphates by Bacteria. A. VAN DELDEN (*Centr. Bakt. Par.*, 1903, 11, 113—119).—*Microspira aestuarii* was cultivated in various solutions containing magnesium sulphate and suitable nutrient material and the amount of hydrogen sulphide produced was estimated. The effect obtained by *M. desulfuricans* is similar to that with *M. aestuarii*. Experiments are described where both organisms were grown in aqueous solutions containing sodium chloride, sodium phosphate, ammonium chloride, sodium lactate and magnesium sulphate—the amount of carbon dioxide and hydrogen sulphide produced being estimated in both cases. In other experiments, sodium malate was substituted for sodium lactate.

The reduction of sulphates by *M. desulfuricans* and *M. aestuarii* is a process which is possible, under anærobic conditions, only in a medium which contains, in addition to sulphates, some suitable organic nutrient material. Sulphate reduction, like denitrification, can be effected in the absence of free oxygen. A. McK.

Influence of Carbohydrates on the Relations of the Gas-exchange in Yeast. [MDLLES.] E. KOLLEGORSKY and O. ZASSOUCHE (*Centr. Bakt. Par.*, 1903, ii, 11, 95—105).—The relation CO_2/O_2 , when dextrose and lævulose are present, first increases, then diminishes, and again increases, always remaining more than 1. Maltose gave similar results. In presence of sucrose, the relation, which is at first less than 1, increases continuously.

Cultures of *Saccharomyces cerevisiæ* containing glycerol gave a relation CO_2/O_2 above 1; whilst in cultures of *Schizosaccharomyces Pombe* the relation was below 1. With mannitol, the relation CO_2/O_2 was below 1. N. H. J. M.

Sterilisation of Drinking Water by Chlorine and Bromine. FRANZ BALLNER (*Arch. Hygiene*, 1903, 48, 140—178).—Experiments are described where cholera germs were added to drinking water, which was then treated with a dilute acidified solution of bleaching powder; the cholera germs were entirely destroyed. Other experiments with various pathogenic micro-organisms are fully described. A. McK.

Influence of Light on Organic Substances, with Special Reference to the Automatic Purification of Streams. RUDOLF RAPP (*Arch. Hygiene*, 1903, 48, 179—205).—The influence of sunlight on oxalic acid solutions of varying concentrations was examined. Air, oxygen, and hydrogen were respectively passed through the solutions, which were exposed in vessels of different shapes, and the amount of carbon dioxide formed was estimated. Whilst the influence of sodium phosphate, hydrochloric, sulphuric, and phosphoric acids on the decomposition was slight, the addition of normal salts, such as sodium chloride, potassium nitrate, &c., considerably increased the amount of oxidation. When the oxalic acid solutions were made turbid by the addition of a little milk, the oxidation was lessened. Sterilised solutions of aspartic acid, uric acid, hippuric acid, carbamide, peptone, tyrosine, leucine, cresol, and phenol, in the presence of air

suffered alteration in sunlight, whilst lactic acid, glycine, and creatine were unaltered. Hippuric acid, peptone, cresol, phenol, and leucine in an atmosphere of hydrogen, were also affected by light.

Experiments with algæ in water contaminated with *Bacillus coli* indicated the function of the former in connection with the automatic purification of streams, when the action of sunlight favours the destruction of bacteria and the growth of organisms containing chlorophyll.

A. McK.

[Action of Antiseptic and Insecticidal Agents.] MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1903, 137, 953—956).—The principal antiseptic and insecticidal agents fall into three main classes; mineral poisons, which form compounds inimical to life; asphyxiating vapours, such as carbon disulphide, hydrocyanic acid, &c.; phenols, and compounds capable of exerting a catalytic action. To the last group belong the terpenes, camphor, aldehydes, &c. Naphthalene, which is commonly regarded as a powerful insecticide, is almost without action.

C. H. D.

Influence of Mineral Food in the Production of Sexes in Dioecious Plants. ÉMILE LAURENT (*Compt. rend.*, 1903, 137, 689—692).—The results of an experiment with spinach, in which exclusively male and female plants were produced, showed that nitrogenous manure and lime both increased the proportion of male plants, whilst potassium and phosphoric acid were favourable to the production of female plants. In absence of any manure, the numbers were about equal (50·7 : 49·3). Small seeds nearly always produced more male plants than larger seeds.

Seeds obtained under the influence of excessive amounts of nitrogen yielded more female than male plants, whilst excesses of potassium, calcium, and phosphoric acid predispose the seeds to yield an excess of male plants.

No effect was observed in the case of hemp and *Mercurialis annua*.

N. H. J. M.

Anærobic Changes in Seeds in Potassium Nitrate Solutions. A. J. NABOKICH (*Chem. Centr.*, 1903, ii, 1012; from *Ber. bot. Ges.*, 21, 398—403).—When peas are immersed in water, a 1 per cent. solution of dextrose, a 0·5 per cent. solution of potassium nitrate, or a 1 per cent. solution of peptone, the ratio of the alcohol to the carbon dioxide formed by a process of intramolecular respiration is almost constant. Respiration takes place most vigorously in peptone and sugar solutions; potassium nitrate solution reduces it to half that observed in water, and after 8 to 10 days it entirely ceases. Considerable differences in the quantities of the so-called non-volatile acids are found, but they can scarcely be ascribed directly to the fermentation process. The combustion of the alcohol by the oxygen of the nitrate is not possible in the case of cultures which lived 7 days. Small quantities of nitrogen trioxide were detected, and this doubtless determines the end of the fermentation. It is doubtful, however, whether the increase in the

quantity of total acid observed in cultures after 14 days is to be ascribed to the presence of nitrous acid. E. W. W.

The Behaviour of Fat in Germinating Oil-containing Seeds. OTTO VON FÜRTH (*Beitr. chem. Physiol. Path.*, 1903, 4, 430—437).—In certain stages there is a breaking up of fat into glycerol and fatty acid. The main thesis of the paper is, however, the probable transformation of fat into carbohydrate, and the possible intermediate stages in the process. W. D. H.

Normal and Intramolecular Respiration of Chlorothecium Saccharophilum. WLADIMIR PALLADIN (*Centr. Bakt. Par.*, 1903, 11, 146—153).—*Chlorothecium saccharophilum* was cultivated in an aqueous solution containing ammonium phosphate, potassium phosphate, magnesium sulphate, calcium chloride, and a trace of ferric chloride, to which dextrose, sucrose, raffinose, and mannitol were respectively added. The amount of carbon dioxide evolved during the growth of the alga in air or in absence of air was estimated; the respiration coefficient ($\text{CO}_2 : \text{O}_2$) was also determined. *Chlorothecium saccharophilum* is a typical aerobic organism; its respiration coefficient is smaller than 1; its growth is possible only in presence of oxygen. In the absence of an atmosphere of oxygen, the alga continues to evolve carbon dioxide; after the cessation of this evolution, the alga is still alive, since, when brought again into air, the carbon dioxide evolution again begins.

The formation of carbon dioxide in an atmosphere free from oxygen is not regarded, in the case of this alga, as a typical fermentation, but rather as intramolecular respiration. A. McK.

Transpiration in Green Leaves when the Upper or Under Surfaces are Exposed to Light. ED. GRIFFON (*Compt. rend.*, 1903, 137, 529—531. Compare Abstr., 1902, ii, 624).—Transpiration diminishes when leaves are reversed, owing partly to the rate at which water is given off being greater than that at which it is renewed. In enclosed leaves, transpiration is diminished, but it is greater when the under sides are exposed to light than when the upper sides are exposed. In the case of cut leaves (enclosed), transpiration is less when the under sides are exposed to light.

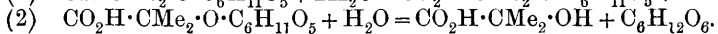
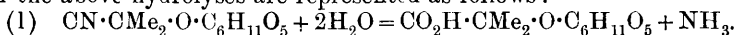
Whilst the pallisade tissue promotes chlorophyllous assimilation, it tends to reduce, and also to control, transpiration in leaves exposed to light. N. H. J. M.

Effect of Temperature on the Assimilation of Carbon Dioxide by Leaves. GABRIELLE L. C. MATTHAEI (*Proc. Roy. Soc.*, 1903, 72, 355—356).—The assimilation of carbon dioxide by single cherry laurel leaves was determined at temperatures varying from -6° to 45° . There are numerous facts to be taken into account, such as amount of illumination, season of the year, &c. There is a maximum assimilation specific to each temperature, but at high temperatures rapid decline of vitality rendered approximate values alone possible. During assimilation, the temperature of the leaf rises. W. D. H.

Cyanogenesis in Plants. Part III. Phaseolunatin, the Cyanogenetic Glucoside of *Phaseolus lunatus*. WYNDHAM R. DUNSTAN and THOMAS A. HENRY (*Proc. Roy. Soc.*, 1903, **72**, 285—294. Compare *Abstr.*, 1902, ii, 578).—When the finely-ground beans from wild *Phaseolus lunatus* are exhausted with cold methylated alcohol, a glucoside *phaseolunatin*, $C_{10}H_{17}O_6N$, is obtained which, on recrystallisation from water, forms spreading rosettes of colourless needles, melting at 141° and having $[\alpha]_D - 26.2^\circ$.

When the glucoside is hydrolysed by acids, dextrose, acetone, and hydrogen cyanide are produced, the amount of dextrose varying in four experiments from 64.6—70.4 per cent. The equation $C_{10}H_{17}O_6N + H_2O = C_6H_{12}O_6 + COMe_2 + HCN$ requires the production of 72.5 per cent. of dextrose.

Hydrolysis of phaseolunatin by alkali hydroxides leads to the production of ammonia and the formation of a new acid glucoside, *phaseolunatinic acid*. The latter substance, when hydrolysed by acids, yields α -hydroxyisobutyric acid and dextrose. Hence phaseolunatin is the dextrose ether of acetone cyanhydrin, and the changes occurring in the above hydrolyses are represented as follows:



Evidence of the existence of phaseolunatin in Rangoon beans has also been obtained.

When the powdered beans from the wild *P. lunatus* are moistened with cold water, the odour of hydrogen cyanide is perceived. It can be shown that the hydrogen cyanide does not exist as such in the plant, but is derived from the glucoside by the action of an enzyme. This enzyme has been isolated in the usual manner, and is probably emulsin.

The seed obtained from *P. lunatus* under cultivation does not contain phaseolunatin, and the reason for this is probably the stimulus to metabolism resulting from improved nutrition and environment.

J. C. P.

Salicylic Acid a Normal Constituent of Wild Cherries.

CHARLES J. A. JABLIN-GONNET (*Ann. chim. anal.*, 1903, **8**, 371—372).—The author states that the juice of wild cherries gives the salicylic acid reaction, and contains as much as 20 or 30 milligrams of this substance per litre. As this juice is frequently used to impart colour to other fruit juices, the presence of mere traces of salicylic acid need not necessarily be looked on as a wilful addition.

L. DE K.

Occurrence of Salicylic Acid in Berries and Stone Fruits.

PAUL SÜSS (*Chem. Centr.*, 1903, ii, 841; from *Verh. Vers. Deutsch. Naturf. Aertze*, 1902, ii, 102—104).—The author examined strawberry juice and strawberry pulp from the various kinds of strawberries growing in the neighbourhood of Dresden, and in every case a reaction for salicylic acid was obtained. One litre of the juice contained from 2 to 3 milligrams of this acid, which, therefore, may be regarded as a normal constituent. This, however, does not interfere much with the

testing for salicylic acid added as a preservative, because for this purpose a much larger amount is required, and this may be isolated by a direct extraction with ether, &c., and estimated colorimetrically.

In the juice of red currants, gooseberries, blackberries, raspberries, cranberries, cherries, plums, greengages, apples, and pears, salicylic acid could not be detected; neither was it present in the oil extracted from raspberry stones by means of ether.

L. DE K.

Natural Occurrence of Salicylic Acid in Berries. FRANZ UTZ (*Chem. Centr.*, 1903, ii, 841; from *Oesterr. Chem. Zeit.*, 6, 385—386).—Strawberries and raspberries gave an unmistakable reaction for salicylic acid when tested by Windisch's process (*ibid.*, ii, 124), but no sign of it was shown by red currants, gooseberries, or bilberries. The author agrees with Windisch that the bulk of the salicylic acid in strawberries and raspberries is present as an ester. As Traphagen and Burke (*Abstr.*, 1903, ii, 388) have found salicylic acid in most other fruits, the author believes that this is due to local influences.

L. DE K.

Saponins of the Seeds of *Entada Scandens*. LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1903, 241, 614—616).—The powdered seeds were freed from fat with ether and then extracted with alcohol; the alcoholic extract was cooled and mixed with ether. The substance which separated was dissolved in water and treated with aqueous barium hydroxide. A small precipitate formed; this was suspended in water and decomposed with carbon dioxide; the solution, filtered from the barium carbonate that had formed, left on evaporation a small amount of a saponin, *a*, which formed a lather with water and was decomposed by boiling with dilute acids, yielding an insoluble sapogenin and a solution which reduced Fehling's solution.

From the barium hydroxide solution, another substance, *entada saponin-b*, which yielded a lather with water, was obtained and purified. This was amorphous and contained ash, 1.6; C, 49.7; H, 6.1 per cent. ($C_{15}H_{22}O_{10}$). It forms a *triacetyl* derivative, and it is hydrolysed by 10 per cent. hydrochloric acid, yielding a sugar (galactose), the phenylhydrazine of which melts at 194°, a crystalline *sapogenin*, $C_{30}H_{50}O_6$, and an amorphous substance.

C. F. B.

Xanthine Derivatives from Plants. TH. WEEVERS and (Mrs.) C. J. WEEVERS-DE GRAAFF (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 203—208).—The following plants, *Coffea arabica*, *C. liberica*, *C. stenophylla*, *Thea assamica*, *T. sinensis*, *Kola acuminata*, *Theobroma cacao*, were examined for caffeine and theobromine at different stages of their development, with the view of determining whether those substances were intermediate or final products of the internal mutation of the plants.

Caffeine and theobromine are present in all the young parts of the plants which grow above ground, even when the plants spring from old parts quite devoid of these substances; during the initial growth

caffeine or theobromine is always formed, but the amount diminishes during further growth of the plant, until finally, in the full-grown plant, no caffeine or theobromine is present. A. McK.

Occurrence of Invertase in Plants. JOSEPH H. KASTLE and MARY E. CLARK (*Amer. Chem. J.*, 1903, 30, 422—427).—Nineteen species of plants, representing fourteen different families, have been examined for the presence of invertase. The results of the investigation are collected in tabular form. They show that invertase is a ferment of wide, if not universal occurrence in the vegetable kingdom, and that in the several organs of plants it is more frequently present than diastase and occurs abundantly in the leaves. It has been found to be present in the growing tubers of the potato and artichoke and in the sprouts of the potato in larger amount than either inulase or diastase. Invertase is not confined to those plants which store up sucrose as the characteristic reserve material, but is found abundantly in those plants which store up starch and inulin, and, moreover, in the very organs which accumulate these reserve materials. E. G.

The Sap of *Asclepias Syriaca*. J. MAREK (*J. pr. Chem.*, 1903, [ii], 68, 385—416).—The sap of *Asclepias syriaca* has a sp. gr. 1·0280—1·0352 at 15°/15°, is slightly acid towards litmus, has a sharp flavour, and an odour resembling that of the flowers, becomes viscous on drying, and coagulates slowly at 38°, rapidly at 90°. On evaporation, the sap leaves a solid residue (16·23—17·73 per cent.), which, on ignition, smells of caoutchouc, evolves inflammable gases, and leaves an ash (1·24 per cent.) containing chlorides, sulphates, phosphates, carbonates, and silicates of sodium, potassium, calcium, magnesium, iron, and aluminium.

The sap contains 0·25 per cent. of nitrogen, equivalent to 1·56 per cent. of albumin, and reduces Fehling's solution equivalent to 0·82 per cent. of glucose. On addition of water, the sap yields a white, curdy precipitate (10·76 per cent.), which consists of caoutchouc (1·46 per cent.) and a mixture of esters of butyric acid, which could not be completely purified. The results of analysis point to the presence of three esters, $C_{24}H_{39}O \cdot C_4H_7O$, $C_{26}H_{43}O \cdot C_4H_7O$ or $C_{25}H_{41}O \cdot C_4H_7O$, and $C_{20}H_{33}O \cdot C_4H_7O$ or $C_{19}H_{31}O \cdot C_4H_7O$, the first two of which melt respectively at 40—45°, and 55—60°; on hydrolysis, these esters yield butyric acid and hydroxylic compounds which give mixtures of benzoyl derivatives. G. Y.

Coca-Leaves. C. HARTWICH (*Arch. Pharm.*, 1903, 241, 617—630).—A paper chiefly of botanical interest. The percentage of alkaloids in the leaves of several varieties of *Erythroxylum Coca* was determined with the following results. Typical: from Cuzco, 0·91; Huanta, 0·86; Ceylon, 0·83. Var. *Spruceanum*: from Truxillo, 0·78; Java, 1·22. The numbers refer to the dry leaves, which originally contained 10—15 per cent. of water. C. F. B.

Composition and Pharmacological Action of Cranberry Leaves. ARTH. KANGER (*Chem. Centr.*, 1903, ii, 893; from *Arch. exp. Path. Pharm.*, 50, 46—75).—This investigation arose from the statement that cranberry leaves have a powerful anti-rheumatic action. The leaves contain proteid, traces of tartaric acid, abundance of quinic acid, quinol, arbutin, and a tannic acid having the formula $C_{28}H_{29}O_{10}$; the latter yields quinol when fused with potash and subjected to dry distillation. In the aqueous extract of the leaves, gallic acid, ellagic acid, ericinole, and ericolin were also found. The gallic and ellagic acids are not present as such in the leaves, but arise from the decomposition of tannic acid. The fruit contains much free benzoic acid, and the flowers, quinol. In large doses, the leaves act as a diuretic and are toxic; this is due to quinol, which is also an antiseptic. Arbutin and quinol pass in part through the body unchanged and appear in the urine.

W. D. H.

Examination and Evaluation of Horse-chestnuts. ERNST LAVES (*Chem. Centr.*, 1903, ii, 1133—1134; from *Verh. Vers. Deutsch. Naturf. Aerzte.*, 1902, ii, II, 660—664).—Dried horse-chestnuts contain on an average 8.5 per cent. of nitrogenous substances, 7.0 of crude fat, 77.2 of non-nitrogenous extractive substances, and 4.7 of fibrous material, and yield 2.6 per cent. of ash. The peeled nuts contain only 1.2 per cent. of fibrous matter. The ash is alkaline and contains 26 per cent. of P_2O_5 , almost wholly combined in inorganic compounds, and 56 per cent. of K_2O . The nitrogenous substances are soluble for the most part in water or in a solution of sodium chloride. The crude fat, which also contains the bitter principle of the chestnut, may be separated into a brown resin and a green, tasteless oil by means of light petroleum. The former is almost insoluble in alkalis. The seeds contain 6 per cent. of the oil, which is a non-drying oil and has an iodine number 108. The resin reduces Fehling's solution and forms dark red and green colorations with Millon's reagent and ferric chloride respectively; it probably contains æsculetin. The non-nitrogenous substances consist of 50 per cent. of insoluble carbohydrates, 14 of sucrose, 13 of glucosides, and 0.2 of tannin. *Aphrodaescin*, $C_{52}H_{82}O_{23}$, is the principal glucoside and forms an amorphous substance which has the same physiological action as a saponine, but its chemical behaviour differs in several respects from those of members of the saponin group. The alcoholic extract of the nuts (Flügge, Ger. Pat. 114845) contains about 36 per cent. of glucosides, 4 of resin (bitter principle), and 6 of fat, and is useful for external application in cases of rheumatism and affections of the skin. The carbohydrates of the glucosides have been fermented; 100 kilograms of seed yielded 25 litres of spirit, the aroma of which resembled that of corn brandy, but was much stronger. The method described in the patent also yields a fatty, nitrogenous fodder which does not contain bitter principles, and a deposit containing phosphoric acid, potassium compounds, and nitrogenous substances.

E. W. W.

Fatty Substances and Acidity of Flours. BALLAND (*Compt. rend.*, 1903, 137, 724—725).—The fatty substance of fresh flour con-

sists of a very fluid oil and a mixture of solid fatty acids. The oil gradually diminishes in quantity and finally disappears, whilst the fatty acids remain. This change enables old flour to be distinguished from new flour. The fatty acids themselves disappear in time and will not be found in very old flour. Hard wheat yields flour containing more acids than soft wheat. The latter should therefore be selected if the flour has to be kept for a long time. N. H. J. M.

Some Ancient Breads. LÉON LINDET (*Compt. rend.*, 1903, 137, 664—666).—Fragments of bread discovered at Pompeii present the appearance of porous charcoal and contain 2.65 per cent. of nitrogen combined with carbon, traces of humous matter yielding acetic acid on dry distillation, and chlorine.

The bread obtained from lake dwellings contains 2.46—4.69 per cent. of nitrogen combined with carbon; starch grains and fragments of the epidermis of the barley can be detected in some specimens.

Bread from the Egyptian tombs is in an excellent state of preservation and contains 11.25 to 11.44 per cent. of nitrogenous matter, and 65.2 to 68.0 per cent. of starch, of which 20.4 per cent. is in the form of soluble starch and dextrin, the remainder as swollen starch; chlorides and nitrates are also present.

In a specimen of fossil bread from Aosta a few wheaten starch grains can be detected. M. A. W.

Rice Oil. CHARLES A. BROWNE, jun. (*J. Amer. Chem. Soc.*, 1903, 25, 948—954).—The constants of a specimen of rice oil are given; the acid number was 166.2, corresponding with 83.5 per cent. of free oleic acid. The oil from fresh rice bran was only slightly acid, but, when the bran was left for some considerable time, a rapid development of acidity took place in the oil, and this may be due either to oxidation or to the action of lipase. Experiments are described which show that a fat-splitting enzyme is present in rice bran. Feeding experiments were also made as to the digestibility of rice oil and the effect of digestion on the composition of rice oil. A. McK.

Sesamé Oil. HANS KREIS (*Chem. Zeit.*, 1903, 27, 1030—1031).—Those samples of sesamé oil which yield azo-dyes become emerald-green on being shaken with nitric acid (1:4), whilst other samples, which do not yield azo-dyes, become orange-red with nitric acid. Indications were obtained of the presence in sesamé oil of a small amount of a phenol (which was not isolated).

When sesamé oil is shaken with 75 per cent. sulphuric acid and a little hydrogen peroxide, an intense olive-green coloration appears, which changes to a bright yellow with green fluorescence on diluting the solution with water. A. McK.

Composition of Milk. H. DROOP RICHMOND (*Analyst*, 1903, 28, 289—292).—The average monthly composition of 12,914 samples of milk analysed during 1902 is given. The average percentage of fat for the year was 3.82. One hundred and ninety-seven samples from

consecutive milkings of one cow were examined. The solids-not-fat varied but little, whilst the fat showed considerable variations. A low percentage of fat, however, was always followed at the next milking by a quantity well above the average.

With regard to the amount of nitrogen in milk, results are recorded where the nitrogen falls appreciably below 0.5 per cent., the lowest percentage obtained in a genuine milk being 0.455.

A method is given for detecting blood in milk, consisting in heating the sample to 50° and centrifugalising, when the blood readily separates. The usual tests may then be applied. W. P. S.

Influence of Variations in the Amount of Soil on the Yield and Composition of Plants. OTTO LEMMERMANN (*J. Landw.*, 1903, 51, 279—285).—The results of experiments with mustard grown in large and smaller pots respectively, showed that more growth was obtained with the larger than with the smaller pots. As the sand in which the plants were grown could not furnish any nutritive matter, the increased yield in the larger pots must be due to the greater space available for root-development. N. H. J. M.

Influence of the Amount of Water in the Soil on Crops and on the Development of Various Varieties of Cereals. CONRAD VON SEELHORST and W. FRECKMANN (*J. Landw.*, 1903, 51, 253—269. Compare Abstr., 1902, ii, 42, 524).—The different cereals and the different varieties of the same cereal are affected in different degrees by variations in the percentage of moisture in the soil.

Oats and one variety of barley produced relatively more grain when the amount of water in the soil was increased. In the case of summer wheat and with two varieties of barley, the relatively greatest amount of grain was obtained when the soil contained 55 per cent. of the absolute moisture; with increased moisture, the relation of grain diminished.

The percentage of nitrogen in the crop depends a good deal on the yield and so indirectly on the amount of water in the soil. In the case of barley, however, there was a difference in the percentage of nitrogen independent of the yield, one variety having a higher percentage of nitrogen than the other two notwithstanding that the yield was greater. N. H. J. M.

Effect of Lime and Marl on the Yield of Potatoes and on the Amount of Nitrogen and Mineral Substances. RICHARD ULBRICHT (*Landw. Versuchs-Stat.*, 1903, 59, 1—25. Compare Abstr., 1902, ii, 581).—Lime and marl increased the yield of tubers and of dry matter in the tubers; the yield of leaf was increased more than the tubers. The amounts of nitrogen in the leaves and tubers were respectively increased and diminished by lime and marl. The lowest amounts of phosphoric acid in leaves were obtained when lime was absent from the soil; in the dry matter of the tubers, the differences in the amounts of phosphoric acid were hardly appreciable. The amount of potassium in the leaves was increased by lime and marl, whilst in the tubers it was generally diminished.

Application of lime alone resulted in leaves containing more calcium and less magnesium than when both lime and marl were applied. The amount of calcium in the leaves diminished when increasing amounts of magnesite were applied. Within certain limits, magnesium may take the place of calcium. In the case of the tubers, no increase in the amount of magnesium and decrease of calcium took place.

N. H. J. M.

Influence of Manuring on the Quality of the Beet. KARL ANDRLÍK (*Zeit. Ver. deut. Zuckerind.*, 1903, 572, 895—905).—The results of the author's experiments, given in detail in this paper, are briefly as follows: moderate amounts of phosphoric acid (in the form of superphosphate, Thomas meal, &c.) have only a slight influence on the yield, which is, however, increased when larger quantities of the phosphate are applied. Chili saltpetre, whether in large or small amounts, influences the quality and yield of beet favourably. When applied in quantities of 50 to 150 kilos. per hectare, potash in the form of chloride, or, better, sulphate increases the yield of beet and also the amount of sugar. Chili saltpetre and superphosphate together have a more favourable action than either alone. With heavy manuring, which increases the yield considerably, a low quality of beet is obtained. Potassium chloride and superphosphate together, when applied in moderate amount, improve the quality of the roots. Thomas meal and mineral phosphate also increase the amount of sugar. Moderate applications of potassium chloride, Chili saltpetre, and a phosphate give very satisfactory results, and the assimilation of the food materials by the roots is, in this case, more complete than with other manurings.

T. H. P.

Amount of Increase of the Dry Matter, Sugar, and Nitrogenous Constituents of Mangels at Different Periods of Growth. J. ARTHUR LE CLERC (*Landw. Versuchs-Stat.*, 1903, 59, 27—81).—Total nitrogen, nitrogen as proteids, amides, and nitrates were determined in mangels at fourteen different dates (June 6th to October 30th), and sugar at nine different periods, commencing July 28th. The same constituents (except sugar) were determined in the leaves and heads at three different dates (August 18th to October 30th). In one sample (November 11th), the determinations were made in three sections, representing the upper, middle, and lower portions of the roots.

The percentage of water in the roots varied with the rainfall, and highest percentage of sugar was found during the period in which the light was strongest. This was followed by a fall in the percentage of sugar, attributed to the young leaves utilising more sugar than they could produce.

Of the three sections of the roots, the upper third contains the most water and nitrogen and the least sugar, the lower third the most dry matter and sugar. The heads contained considerable amounts of sugar.

As regards the relation of sugar to nitrogen, the increase in the

former is much more rapid than in the latter. During the earlier periods, nearly half the nitrogen of the roots, and about one-third of the leaves, is present in insoluble forms.

The proteid nitrogen (precipitated successively by copper hydroxide and lead acetate) amounted to 27 to 39 per cent. of the total nitrogen. The amounts of nitrates depended on the rainfall. The amide nitrogen in the roots amounted to 4 per cent. of the total at the commencement, and rose in the fourth period to 12 per cent., and then remained constant. The leaves contained much less amides (2—4 per cent. of the total nitrogen).

Aspartic and glutamic acids could not be detected, and it is thought probable that the amino-acids are chiefly leucine and tyrosine.

N. H. J. M.

Ammonium Sulphate and Organic Nitrogen compared with Sodium Nitrate. PAUL WAGNER, R. DORSCH, F. ASCHOFF, H. RUTHS, and G. HAMANN (*Bied. Centr.*, 1903, 32, 728—737; from *Arb. Deut. Landw. Ges.*, 1903, Heft. 80. Compare Abstr., 1902, ii, 43).—Addition of farmyard manure, both alone and in conjunction with sodium nitrate, to garden soil resulted in a loss, followed by an increase, in the total amount of nitrates. In the soil alone, and in soil to which sodium nitrate alone was added, the amounts of nitrates remained constant the whole time (64 days). In another experiment, application of farmyard manure to soil diminished the amount of nitrate present, whilst when ammonium salts were added (in addition to farmyard manure) the reduction in the amount of nitrates was limited to the first 12 days (instead of 96 days), and was followed by a considerable increase until 96 days had passed, after which the amount of nitrates again diminished.

The results of field experiments showed that the average yield of oats, barley, wheat, rye, potatoes, sugar-beet, and mangels was 70 when manured with ammonium salts, as compared with sodium nitrate = 100. Of the total nitrogen, 43 per cent. was utilised by the crop when ammonium sulphate was employed, and 62 per cent. with sodium nitrate. Ammonium salts gave better results than sodium nitrate in the case of barley and oats.

N. H. J. M.

Manurial Experiments with Precipitated Calcium Phosphate. HENRIK G. SÖDERBAUM (*Bied. Centr.*, 1903, 32, 737—745; from *Med. kongl. Landsbr.-Akad. Exper.*, 1902, Nos. 75 and 78. Compare Abstr., 1902, ii, 350).—By altering the process by which the phosphoric acid of apatite is rendered more readily available, it is possible to obtain dicalcium phosphate (containing 37.23 per cent. of phosphoric acid soluble in 2 per cent. citric acid) instead of tricalcium phosphate.

The results of experiments with oats and peas showed that the dicalcium phosphate is equal in manurial effect to superphosphate, and that the simultaneous application of calcium carbonate has very little effect unless the amount of phosphate is small.

In conjunction with tricalcium phosphate, and especially with bone

meal, calcium carbonate produced a very great reduction in the yield of oats. With superphosphate, calcium carbonate only diminished the yield with small application of phosphoric acid, and was beneficial in presence of large amounts of phosphate. N. H. J. M.

Manurial Value of Bone Meal Phosphoric Acid. HENRIK G. SÖDERBAUM (*Bied. Centr.*, 1903, 32, 745—747; from *Kongl. landsbr.-akad. handl. tidskr. Stockholm*, 1903, 42—53).—The yield of oats, manured with bone meal and calcium carbonate, was 7.36 compared with the yield obtained with superphosphate = 100. Bone meal alone gave a yield of 73.5 per cent. of that obtained with superphosphate.

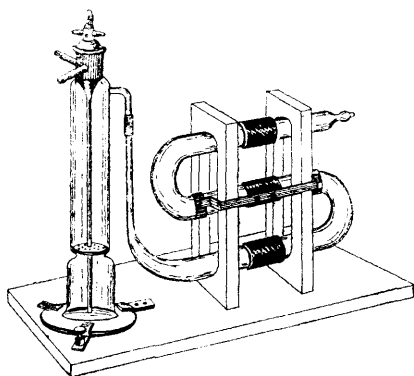
Bone meal in conjunction with sodium nitrate and ammonium sulphate gave better results (with oats) than when the same amount of nitrogen was applied in the form of sodium nitrate. N. H. J. M.

Heating of Bungkil. H. A. C. VAN DER JAGT (*Chem. Centr.*, 1903, ii, 1141; from *Mededeelingen van het proefstation voor suikerriet in West Java "Kagok" te Pekalongan*, No. 66).—The residue left in the hydraulic presses after removing the oil from ground nuts is used as a manure under the name of bungkil. This material, when stored in large quantity, is liable to deteriorate in quality owing to a process of oxidation. The oxidation of certain components to carbon dioxide is effected by means of bacteria and causes the mass to become hot, and even at times to take fire. The temperature reaches a maximum after a certain time and then slowly sinks. Bungkil contains both aerobic and anaerobic bacteria; organisms are also present which become more active at higher temperatures (about 67°), but these play only a secondary part in the process. The changes which occur consist chiefly of the decomposition of proteids, fat, pentosans, and carbohydrates; cellulose is not attacked. E. W. W.

Analytical Chemistry.

A New Drying Apparatus. FRIEDRICH BOLM (*Chem. Zeit.*, 1903, 27, 1037).—The apparatus, which is intended for the purification of air or oxygen used in organic combustions, will be readily understood from the figure. Either gas may be admitted by a single movement of the tap.

The perforated leaden disc is covered with a layer of glass beads, a little cotton wool is introduced, and on this is placed a layer of soda-lime, which is then covered with a thin layer of calcium chloride.



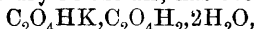
Strong sulphuric acid is then introduced by means of the tube into the lower part of the cylinder, and when it needs renewing it is siphoned off again. The serpentine tube, composed of three pieces (*Zeit. anal. Chem.*, 1899, **38**, 289), may be readily filled and cleaned. L. DE K.

An Apparatus for Extracting Liquids with Ether. FRIEDRICH KUTSCHER and HERMANN STEUDEL (*Zeit. physiol. chem.*, 1903, **39**, 473—476).—The solution to be extracted is placed in a vessel shaped like a test-tube, but constricted at the top to form a long neck. A wide side-tube leads from the bottom of this neck to a flask in which the ether is boiled, the flask and tube being connected by a ground-in joint. The neck of the vessel containing the solution is fitted to a reflux apparatus. The condensed ether falls drop by drop into a tube contained in the extraction vessel and reaching to the bottom of the same. From the lower end of this tube, the ether escapes into the solution, and in rising through the latter is caused, by means of a spiral wound round the outside of the tube, to take a long path through the solution. By the lengthened contact of the ether with the solution, the extraction is hastened. As the ether collects on the surface, it flows through the side-tube into the heating flask. W. P. S.

Apparatus for the Electrolytic Determination of Metals, using a Rotating Cathode. E. S. SHEPHERD (*J. Physical Chem.*, 1903, **7**, 568—570).—Details are given of the apparatus used in the author's laboratory. It does not differ in principle from that described by Gooch and Medway (*Abstr.*, 1903, ii, 613). The author confirms their result that an electrolytic deposition can be carried out much more rapidly when a rotating cathode is employed. J. C. P.

A very Sensitive Indicator from *m*-Toluidine. JULIUS TRÖGER and W. HILLE (*J. pr. Chem.*, 1903, [ii], **68**, 297—309).—See this vol., i, 118.

Potassium Tetroxalate in Volumetric Analysis. OTTO KÜHLING (*Zeit. angew. Chem.*, 1903, **16**, 1030—1032).—The author has proved by a number of experiments that recrystallised potassium tetroxalate, obtained by rapidly cooling and stirring the hot saturated solution, and allowed to dry in the air, has the formula



and may be safely used for standardising purposes.

L. DE K.

Oxidation of Organic Substances with Persulphates in Acid Solution. MAX DITTRICH (*Ber.*, 1903, **36**, 3385—3387. Compare *Abstr.*, 1903, ii, 581).—Aliphatic substances, especially those containing halogen, are decomposed when boiled with acid persulphates; this can be made use of to estimate the halogen in organic substances provided silver nitrate is initially added, and oxidation products of the halogens, such as chlorates and perchlorates formed during the reaction, are subsequently reduced. E. F. A.

Action of Boric Acid on Iodides; its Use for the Separation of Iodine from Iodides in the presence of Bromides and Chlorides. HENRI BAUBIGNY and PAUL RIVALS (*Compt. rend.*, 1903, 137, 650—653).—Whilst pure boric acid only decomposes saturated solutions of bromides and chlorides on heating, it liberates hydrogen iodide from solutions of iodides in the cold, and in the presence of a suitable oxidising agent can be employed for the estimation of iodine in the presence of chlorides and bromides. For this purpose, the dilute saline solution is distilled at a temperature of 45—50° with boric acid and manganese dioxide (prepared by reducing a permanganate by means of alcohol), and the iodide collected in a receiver containing an alkaline solution. Theoretical results are obtained when the boric acid is present in the proportion of 10 grams for every 100 c.c. of the solution, and ten times the quantity of manganese dioxide required by theory is employed. Control experiments with bromides and chlorides gave traces of bromine in the distillate only when the proportions of bromide and boric acid were large; the chlorides were even more difficultly decomposed. M. A. W.

Conditions under which Iodine can be Separated in the form of Cuprous Iodide from a Mixture of Alkali Chlorides, Bromides and Iodides. HENRI BAUBIGNY and PAUL RIVALS (*Compt. rend.*, 1903, 137, 753—756. Compare preceding abstract).—The iodine in a mixture of alkali chlorides, bromides, and iodides can be completely separated as cuprous iodide if excess of copper sulphate is added to the solution, together with an alkaline arsenite and a trace of a ferrous salt. The copper arsenite formed reacts with the liberated iodine to form cuprous iodide according to the equation: $2\text{CuHASO}_3 + \text{I}_2 + 2\text{H}_2\text{O} + 2\text{CuSO}_4 = 2\text{CuHASO}_4 + \text{Cu}_2\text{I}_2 + 2\text{H}_2\text{SO}_4$, whilst the ferrous salt reduces any small quantity of copper iodide that may remain in solution. The reaction proceeds in the cold, the bromides and chlorides undergoing no reduction even after 12 hours. M. A. W.

Separation of Iodides from Chlorides and Bromides in a Mixture of Alkali Halogen Salts by Conversion into Iodic Acid, and Preparation of Pure Iodine. HENRI BAUBIGNY and PAUL RIVALS (*Compt. rend.*, 1903, 137, 927—929).—The solution of mixed halogen salts is rendered alkaline by means of sodium carbonate and the iodide oxidised to the iodate by potassium permanganate. The bromide and chloride are then separately removed from the solution by distillation with copper sulphate and potassium permanganate (*Abstr.*, 1898, ii, 90, 137). The iodine which remains in the mother liquor as iodic acid is estimated as silver iodide by the addition of silver nitrate and subsequent reduction by sulphur dioxide.

Pure iodine (free from chlorine, bromine, and cyanogen iodide) can be prepared by Gay Lussac's method from the solution of the iodate after the elimination of the bromides and chlorides; for this purpose,

five-sixths of the solution are treated with an alkali sulphite to reduce
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the iodate to the iodide and then mixed with the remaining sixth part, when the following reaction occurs : $\text{HIO}_3 + 5\text{HI} = 3\text{H}_2\text{O} + 3\text{I}_2$.
M. A. W.

The Iodine-Tannin Reaction for Hydroxyl Ions. WILHELM VAUBEL (*Zeit. angew. Chem.*, 1903, 16, 1073—1074).—If to a solution of tannin is added a salt and then a particle of solid iodine, a red coloration is noticed with sodium carbonate, sodium hydrogen carbonate, sodium metaborate, disodium hydrogen phosphate, diammonium hydrogen phosphate, potassium cyanide, ammonium carbonate, potassium metantimoniate, sodium acetate, and barium carbonate, also with sodium chloride, sodium nitrate, potassium chloride, potassium bromide, potassium bromate, potassium chlorate, potassium nitrate, ammonium nitrate, ammonium chloride, ammonium carbonate, calcium chloride, barium chloride, barium nitrate, potassium sulphate, and ammonium sulphate, also with all alkaline hydroxyl compounds.

No red colour is obtained with potassium iodide, potassium thiocyanate, or sodium thiosulphate and sodium hydrogen sulphite, or copper sulphate, iron sulphate (blue-black), ferrous chloride (ditto), copper nitrate, mercuric chloride, lead acetate and zinc sulphate, which show a more or less acid reaction, or normal potassium chromate, potassium dichromate, and potassium ferrocyanide.

The reaction is only obtained when hydroxyl ions are present and the intensity increases with the number of hydroxyl ions. Its occurrence with so many so-called neutral salts shows that they have undergone some hydrolytic dissociation, even if only to a slight extent.

L. DE K.

Estimation of Sulphur in Pyrites. GEORG LUNGE (*Ber.*, 1903, 36, 3387—3389).—A reply to Silberberger (*Abstr.*, 1903, ii, 751).
J. J. S.

Exact Estimation of Sulphur in Vegetable and other Organic Substances. W. E. BARLOW (*J. Landw.*, 1903, 51, 289—313).—A modification of Berthelot's method. The substance is heated in a combustion tube first in a current of carbon dioxide and then in oxygen, the gases being passed over heated soda-quartz (prepared by mixing sand with 3—4 grams of sodium carbonate dissolved in water and drying) in the front part of the tube, the end of which, drawn out and turned down, dips into a beaker of water. When the combustion is finished (20—30 minutes), the boat containing the ash is taken out. The soda-quartz, asbestos, &c., are emptied into a dish, into which the tube is then rinsed with water and dilute hydrogen chloride. It is then evaporated to dryness, heated at 110°, stirred with hydrochloric acid, and extracted with water. The sulphate is then precipitated with barium chloride.

The method is easily carried out and gives correct results. All methods in which the substance is first burnt (without or with calcium acetate) are unsatisfactory.

The combustion tube, which is provided with a side-tube to admit oxygen in front of the substance, is figured in the original.

N. H. J. M.

Titration of Sulphuric Acid by Benzidine. WOLF JOHANNES MÜLLER (*Zeit. angew. Chem.*, 1903, 16, 1017).—A controversy with Raschig on the subject of the estimation of sulphates by means of benzidine hydrochloride (*Abstr.*, 1903, ii, 691). L. DE K.

Estimation of Selenium. GIOVANNI PELLINI and E. SPELTA (*Gazzetta*, 1903, 33, ii, 89—92).—The best method for the estimation of selenium is based on the reduction of selenous acid by means of hydrazine: $\text{N}_2\text{H}_4 + \text{SeO}_2 = \text{Se} + 2\text{H}_2\text{O} + \text{N}_2$, as was pointed out by Jannasch (*Abstr.*, 1899, ii, 59). According to the method given by the authors, the nitrogen evolved in this reaction is measured in a modified form of Schultze and Tiemann's apparatus, the gas being collected over boiled water. The selenium dioxide, dissolved in water or very dilute hydrochloric acid, is introduced into the flask of the apparatus, and its volume brought up to 50 c.c.; a few grams of sodium chloride are then added, and the liquid boiled until all the air is driven off. A solution of about 2 grams of hydrazine hydrochloride or sulphate, acidified with hydrochloric acid and previously boiled, is next added. The evolution of nitrogen is soon complete, and stops abruptly, so that the end of the reaction is easily seen. The volume of nitrogen is then measured and reduced to 0° and 760 mm. Small quantities of selenium dioxide can be estimated in this way, since 1 gram of the dioxide yields 201.83 c.c. of nitrogen. Test experiments gave good results.

Tellurium cannot be estimated in this way, as the evolution of nitrogen is very slow and continues for a long time. Neither can selenium be separated from tellurium by means of hydroxylamine, which does not act on selenium dioxide in the way stated by Jannasch (*loc. cit.*), namely, $4\text{NH}_2\cdot\text{OH} + \text{SeO}_2 = \text{Se} + 6\text{H}_2\text{O} + 2\text{N}_2$. T. H. P.

Estimation of Nitrogen by Kjeldahl's Method. S. P. L. SÖRENSEN and C. PEDERSEN (*Zeit. physiol. Chem.*, 1903, 39, 513—525).—This method was found to give good results in the case of creatine, creatinine, lysine compounds, and uric acid. Kutscher and Steudel's statements (*Abstr.*, 1903, ii, 687) that the method is untrustworthy are further combated. W. P. S.

Estimation of Ammonia in Urine. C. DEMON (*J. Pharm. Chim.*, 1903, 18, [vi], 289—293).—The amount of ammonia in urine 24 hours after emission was found to be larger than the quantity present at the time of emission. The increase in some instances amounted to 100 per cent. of the ammonia originally in the urine. The addition of 5 per cent. of sodium fluoride prevented any change taking place, urine thus preserved giving exactly the same results after 24 hours as when fresh. Folin's method (*Abstr.*, 1901, ii, 575) was employed for estimating the ammonia. W. P. S.

Estimation of Ammonia in Urine. OTTO FOLIN (*Zeit. physiol. Chem.*, 1903, 39, 477—478).—It is pointed out that the method described by Krüger and Reich (*Abstr.*, 1903, ii, 688) had been previously published by Schaffers (*Abstr.*, 1903, ii, 180), to whom is

due the idea of adding alcohol to prevent frothing during the distillation. Hausmann's method was found to be untrustworthy for the estimation of ammonia in digestion fluids. W. P. S.

New Reaction of Hydroxylamine. LOUIS J. SIMON (*Compt. rend.*, 1903, 137, 986—987).—The addition of a very dilute alkaline solution of sodium nitroprusside to a solution of hydroxylamine or one of its salts produces on boiling a yellow coloration, deepening through orange to a deep cherry-red and becoming pink on dilution. Nitrogen and nitrous oxide are evolved during the boiling. The tint obtained in a 0.1 per cent. solution of hydroxylamine hydrochloride is sufficiently intense to remain visible after further diluting 1000 times. The coloration in very dilute solutions is, however, largely dependent on the quantity of reagent employed. The reaction is not given by oximes. C. H. D.

Estimation of Nitrates in presence of Nitrogenous Organic Matter. THEODOR PFEIFFER (*Zeit. anal. Chem.*, 1903, 42, 613—617).—The author reaffirms, and brings fresh experiments to prove, the correctness of his statement, that, in presence of ammonium sulphate or urea, Schloesing's method always gives low results, and points out that even the numbers obtained by Liechti and Ritter (*Abstr.*, 1903, ii, 574) confirm this. M. J. S.

Reduction of Nitric Acid in Metallic Nitrates to Ammonia by the Electric Current. WM. H. EASTON (*J. Amer. Chem. Soc.*, 1903, 25, 1042—1044).—Vortmann (*Zeit. anal. Chem.*, 1880, 19, 11) has stated that nitrates may be completely reduced to ammonia by electrolysis in the presence of copper sulphate. As many have failed to get satisfactory results, the author has reinvestigated the process and finds it to be perfectly satisfactory provided the following conditions are adhered to.

Amount of nitrate, about 0.5 gram; copper sulphate, about 0.5 gram; cathode, platinum or copper plate of 100 sq. cm. area; amperes, 0.15 to 3.0; time, $1\frac{1}{4}$ hours for 3, and $8\frac{1}{2}$ hours for 0.15 ampere; volts, from 3 to 8; dilution, 150 c.c.; sulphuric acid of sp. gr. 1.062, 30 c.c. L. DE K.

Reaction for Nitrites. W. A. BLUNT (*Analyst*, 1903, 28, 313).—The addition of potassium ferrocyanide solution to a water containing nitrites causes a urine-yellow tint to appear, due to the conversion of the ferrocyanide into ferricyanide. It is suggested that it might be feasible to use the reaction as a quantitative colorimetric method for estimating nitrites. W. P. S.

Solubility of Magnesium-Ammonium Phosphate in Ammonium Citrate. A. BOLIS (*Chem. Zeit.*, 1903, 27, 1151).—A series of experiments showing that two grams of hexahydrated magnesium ammonium phosphate in contact with 100 c.c. of ammonium citrate solution (containing 400 grams of citric acid per litre) lose on an average 0.457 per cent. of their weight owing to solubility. This will average 0.587 per cent. when working at 50°. L. DE K.

Colorimetric Estimation of [small amounts of] Phosphoric Acid in the presence of Silica. OSWALD SCHREINER (*J. Amer. Chem. Soc.*, 1903, 25, 1056—1062).—The yellow coloration caused by the action of molybdate solution on phosphoric acid may, as is well known, be used for its colorimetric estimation, but the reaction is interfered with by the presence of silica, which also gives a yellow colour. The author, however, has found that whereas the phosphate colour is always the same, that of the silica differs very considerably according to the method of working. On this principle, the following process has been founded. Fifty c.c. of the solution are mixed with 5 c.c. of nitric acid and 4 c.c. of ammonium molybdate solution, and after 20 minutes the colorimetric reading is made. This gives a in the equation (1). Another 50 c.c. are then mixed with 4 c.c. of the ammonium molybdate; after one hour, 5 c.c. of nitric acid are added, and after 20 minutes the reading is made. This then gives b in equation (2).

The equations are (1) $x + y = a$; (2) $\frac{1}{2}x + y = b$, in which x is the silica, and y the phosphate reading, whilst a is the experimental reading under the one, and b that under the other condition.

Preparation of the Standard Colorimetric Solution.—Ten c.c. of a solution of disodium hydrogen phosphate containing 0.0001 gram of phosphoric anhydride per c.c. are diluted to 80 c.c., 9 c.c. of nitric acid of sp. gr. 1.07 are added, and then 8 c.c. of an aqueous solution of ammonium molybdate containing 50 grams of the salt per litre. After diluting to 100 c.c. and waiting for 20 minutes, it is ready for use. Each c.c. of this solution represents 0.00001 gram of phosphoric oxide.

The amount of phosphoric acid may now be readily calculated from the readings.

L. DE K.

Detection and Estimation of Traces of Arsenic in Organs, &c. GABRIEL BERTRAND (*Ann. Chim. anal.*, 1903, 8, 361—369, 415—421).—The substance is repeatedly evaporated with a mixture of 9 parts of nitric acid and 1 part of sulphuric acid, the charred mass is extracted with water and the filtrate mixed with a little sulphurous acid and evaporated to a small bulk. It is then treated for some hours with hydrogen sulphide, the precipitate is washed and dissolved in ammonia, and, after evaporating, the residual arsenious sulphide is freed from any traces of organic matter by a renewed treatment with nitric and sulphuric acids. The arsenical solution thus obtained is then ready for being introduced into the Marsh apparatus.

The nitric acid used in these operations is freed from arsenic by repeated distillation with addition of one-tenth of its volume of sulphuric acid. A modified form of the Marsh apparatus is used. This consists of a 90 c.c. generating flask fitted with a specially constructed stoppered funnel tube, to which is sealed a side-tube admitting carbon dioxide or hydrogen. Platinised zinc is introduced and the air inside the apparatus is swept out, 10 c.c. of dilute sulphuric acid (1:5) are introduced, and the reduction tube is heated. The spray of liquid is practically retained in a bulb before the gas passes through a drying tube filled with desiccated cotton wool, which the author considers to be more effective than calcium

chloride. The arsenical liquid is now introduced and rinsed down with successive small portions of dilute sulphuric acid (1:5); during the operation the current of hydrogen should not exceed 4 or 5 c.c. per minute, which may be gauged by dipping the bent end of the decomposition tube into water. The gases then pass through the reduction tube, which is heated over a length of 10 cm. and is enveloped in a sheet of metal. At a very short distance from the burners, the tube is cooled by the simple device of wrapping a piece of filter paper round it and keeping this moist by allowing water to drip on it from a reservoir. It is on this cold spot that the arsenical mirror will become visible, generally after about 5 minutes, although it may take 1 or even 2 or 3 hours. From the appearance of the mirror, the quantity of arsenic may be judged as usual.

L. DE K.

Determination of the Heat of Combustion by means of Combined Oxygen and Parr's Method. HERMANN LANGBEIN (*Zeit. angew. Chem.*, 1903, 16, 1075—1077).—An adverse criticism of Parr's coal calorimeter (*Abstr.*, 1900, ii, 710), in which the combustion is effected with sodium peroxide.

L. DE K.

Estimation of Carbon Dioxide in Electrolytic Chlorine. C. OFFERHAUS (*Zeit. angew. Chem.*, 1903, 16, 1033—1034).—*1st Method.*—A definite volume of the gas is treated with the usual precautions in $N/2$ sodium hydroxide contained in a Bunte-burette, when the loss in volume represents the joint chlorine and carbon dioxide. Another portion of the gas is then treated with potassium iodide and the liberated iodine estimated by titration and calculated into its equivalent volume of chlorine.

2nd Method.—A definite volume of the gas is absorbed in 45 c.c. of $N/2$ sodium hydroxide, the amount of carbon dioxide in which is accurately known. After introducing into the burette 5—10 c.c. of 3 per cent. hydrogen peroxide and shaking, the liquid is diluted to 200 c.c., and in 50 c.c. the carbon dioxide is titrated by Winkler's process.

3rd Method.—Instead of titrating the carbonic acid, it may be advantageously determined by the gas-volumetric apparatus devised by Lunge and Marchlewski.

L. DE K.

Estimation of Carbon Dioxide in presence of Sulphites, Sulphides, and Organic Substances. U. STANEK and JAK. MILBAUER (*Zeit. Ver. deut. Zuckerind.*, 1903, 572, 958—961).—The author's method consists in passing the gas, evolved by the action of hydrochloric acid on a mixture of carbonate with sulphite or sulphide, over moist, granulated iodine, which frees it from sulphur dioxide or hydrogen sulphide; the iodine vapours carried away by the gas are then removed by means of aluminium turnings and the remaining carbon dioxide dried and absorbed in potash bulbs. A special apparatus has been devised for the estimation. The method is shown to give good results.

T. H. P.

Estimation of Very Small Amounts of Potassium. FRANK K. CAMERON and G. H. FAILYER (*J. Amer. Chem. Soc.*, 1903, 25, 1063—1073).—Briefly, the method is as follows: the potassium is separated in the usual way with platinum chloride, the excess of which is removed by washing with successive small quantities of alcohol. When the alcohol has evaporated, the precipitate is dissolved in hot water, and when cold a drop of hydrochloric acid is added. On now adding potassium iodide, a pink colour is developed which reaches its final intensity in four hours. The liquid is then compared in a suitable colorimeter with a solution containing a known amount of potassium platinumchloride.

If it is desired to work with yellow solutions instead of pink ones, no hydrochloric acid should be added and the mixture should be heated with a little alcohol.

L. DE K.

Titrimetric Estimation of Potassium as Potassium Bismuth Thiosulphate. FRIEDRICH W. KÜSTER and MAX GRÜTERS (*Zeit. anorg. Chem.*, 1903, 36, 325—331).—Potassium bismuth thiosulphate, $K_3Bi(S_2O_3)_3$, is so sparingly soluble in dilute alcohol in comparison with the corresponding sodium salt that a method based on this difference between the two salts was devised by Carnot (*Abstr.*, 1878, 448) for the quantitative separation of sodium from potassium. The authors find, however, that this method is quite unsuitable, since the precipitated potassium bismuth thiosulphate always contains the isomorphous sodium salt as an impurity.

A. McK.

Electrolytic Separation of Silver from Antimony. ARTHUR FISCHER (*Ber.*, 1903, 36, 3345—3350).—Solutions containing silver and antimony salts were electrolysed in presence of tartaric and nitric acids, first using 1.35 volt and, after three hours, 1.4—1.45 volts. The silver is first deposited, and is quite free from antimony, the deposition of which does not begin until 1.5—1.6 volts are employed. The electrolysis may be conducted at the ordinary temperature with a current of 0.05—0.01 ampere, when the separation of silver is complete after 18 hours, or at 50—60° with a current of 0.12—0.02 ampere, when the separation requires 8—9 hours. When the silver has been all deposited, sodium sulphide is added to the solution, which has been made alkaline by sodium hydroxide, and the electrolysis then conducted with 1.3—1.6 volts and 1—1.5 amperes at 60—70°.

The separation may also be conducted with a solution to which tartaric acid and potassium cyanide have been added.

A. McK.

Indirect Estimation of Calcium and Magnesium. The Magnesites of Greece. ANASTASIOS K. CHRISTOMANOS (*Zeit. anal. Chem.*, 1903, 42, 606—612).—On account of the difficulty of effecting an accurate separation of calcium and magnesium by a single precipitation of the calcium as oxalate, the author advocates the indirect method of weighing both metals as carbonates, and then either estimating the carbon dioxide or converting the mixture of carbonates into sulphates.

M. J. S.

Qualitative Separation of Barium, Strontium and Calcium by means of Potassium Dichromate and Ammonia. C. REICHARD (*Chem. Zeit.*, 1903, 27, 1035—1036).—The neutral solution of the three alkaline earths is mixed with a cold saturated solution of potassium dichromate, which precipitates the barium only. Ammonia is carefully added to the filtrate until this turns yellow, when a characteristic precipitate of strontium chromate will gradually form (*Abstr.*, 1903, ii, 757). The calcium is then precipitated with ammonium oxalate.

L. DE K.

Volumetric Estimation of Magnesium. ERWIN RUPP (*Arch. Pharm.*, 1903, 241, 608—613).—An arsenate is best estimated volumetrically by mixing it with dilute sulphuric acid and 3—5 grams of potassium iodide in a long-necked flask, adding a few pieces of glass or platinum, and boiling with the flask in an inclined position until the colour of the iodine has nearly disappeared. The solution is then diluted with a little water, the iodine remaining is removed by adding sulphurous acid, the excess of the latter is removed by boiling, and the solution is cooled, mixed with a slight excess of sodium hydrogen carbonate, and titrated with *N*/10 iodine solution.

For the estimation of magnesium, the solution of the salt is added to a solution containing ammonium chloride, ammonia, and a measured quantity (in excess) of an arsenate solution of known strength, both solutions being boiling. The solution is diluted to 100 c.c., shaken frequently for a time, and allowed to remain twelve hours in all, after which it is filtered from the precipitate of magnesium ammonium arsenate and the excess of arsenate determined in 50 c.c. of the filtrate as described above. One c.c. of an *N*/10 solution corresponds with 0.001218 gram of magnesium. In six experiments, the error varied between -0.7 and +0.9 per cent. of the quantity estimated.

Barium can be estimated in a similar manner.

C. F. B.

Detection of Zinc in Cases of Poisoning. DIOSCORIDE VITALI (*L'Orosi*, 1902, 25, 145—148).—The author points out that when testing for zinc in animal organs and making use of potassium chlorate for the destruction of the organic matter, it is important to ascertain that the chlorate employed is free from zinc, as one of the methods for manufacturing it consists in treating zinc oxide with chlorine and heating the product of the reaction with potassium chloride.

T. H. P.

Use of Litharge in Dry Lead Assaying. A. COPPALLE (*Ann. Chim. anal.*, 1903, 8, 412—415).—When dealing with very poor lead ores, it is customary to add a known weight of litharge so as to get a larger button. The quantity of lead contained in the litharge, which has been ascertained by a separate experiment, is then deducted from the weight of the button. The author states that it is very important when assaying this litharge to flux it with addition of the same kind of gangue as is contained in the ore to be analysed, particularly when dealing with samples of galena.

L. DE K.

Separation of Cerium by means of Potassium Permanganate. C. RICHARD BOEHM (*Zeit. angew. Chem.*, 1903, 16, 1129—1132).—For technical purposes cerium may be separated from the accompanying elements by boiling with potassium permanganate in the presence of sodium hydroxide. An excess of the latter should, if possible, be avoided, so as to precipitate the cerium only, the amount of permanganate being regulated by a preliminary experiment. The precipitate is washed by decantation with water, and then treated with water containing 10—20 per cent. of nitric acid to dissolve any of the other earths that may have been precipitated. The residue then contains, besides manganese dioxide, the bulk of the cerium as dioxide, which may be extracted by heating with stronger acids. L. DE K.

Behaviour of Cerium, Lanthanum, Neodymium, Praseodymium, Thorium, and Zirconium towards Organic Bases. BURT L. HARTWELL (*J. Amer. Chem. Soc.*, 1903, 25, 1128—1136. Compare Jefferson, *Abstr.*, 1902, ii, 534).—With the view of separating thorium and zirconium from cerium, lanthanum, neodymium, and praseodymium, the behaviour of a large number of organic bases towards salts of cerium, &c., was studied. For the separation of thorium from zirconium, the chloroanilines and hexamethylenetetramine appeared the most suitable of the bases tried, whilst *p*-toluidine gave promising results in the separation of zirconium and thorium from lanthanum, neodymium, and praseodymium. A. McK.

Method of Estimating the Amounts of the Oxides of Didymium and Erbium by means of the Absorption Bands of their Solutions, and its Application to other Solutions. JOHN E. PURVIS (*Proc. Camb. Phil. Soc.*, 1903, 12, 202—205).—A spectroscope is so arranged that the absorption spectra of two solutions, one of known, the other of unknown strength, can be carefully compared. The vertical vessel containing the solution of known strength is provided with a hollow cylinder closed with a glass plate; this cylinder is moved up or down until the intensities of the absorption bands of the two parallel spectra are identical. The concentrations of the solutions are then inversely as the thicknesses producing the absorptions, and hence, as is shown in the paper, it is possible to estimate very satisfactorily the amount of didymium and erbium in the solution of unknown strength. J. C. P.

Electrolytic Estimation of Manganese and its Separation from Iron and Zinc. GEORGE P. SCHOLL (*J. Amer. Chem. Soc.*, 1903, 25, 1045—1056).—Manganese and iron may be estimated simultaneously by electrolysing the sulphate solution in the presence of ammonium acetate and formic acid. Zinc and manganese may be similarly separated in the presence of formic acid and ammonium formate. The iron or zinc are deposited as metals at the cathode, whilst the manganese is precipitated as peroxide on the anode. For working details, the original paper should be consulted. L. DE K.

Occurrence of Iron and Manganese in Service Water. ED. VON RAUMER (*Zeit. anal. Chem.*, 1903, 42, 590—602).—It appears to be probable that the difficulties which have been occasioned in various continental water services by the growth of *Crenothrix polyspora* in the water pipes, with the resulting formation of ferruginous deposits, which produce obstructions, are only encountered when the iron in the water is in combination with organic (humous) acids. *Crenothrix*, being absolutely free from chlorophyl, is incapable of assimilating purely inorganic materials, and it has been found that processes of purification from iron, which deal only with the inorganic compounds of that metal, have not prevented the growth of the alga. In the estimation of iron in a water supply, it is therefore necessary to destroy the organic matter, and this has not been done in some of the older processes (for example, Jolles' colorimetric method). All filtrations of the iron solution must also be avoided, as it is practically impossible to wash out the iron completely from a cellulose filter, and the use of an asbestos filter is precluded by the fact that the iron silicates, which are often present, are slowly attacked by hot acids. The author evaporates 10—20 litres of the water to dryness with addition of a little sulphuric acid and potassium hydrogen sulphate, fuses the residue, dissolves it in dilute sulphuric acid, boils to expel any sulphurous acid which may have been formed, reduces with zinc, and titrates with permanganate. The presence of a white turbidity in the solution (silica, calcium sulphate, &c.) rather assists the observation of the end-point.

Besides the occurrence of obstructions in water pipes occasioned by ferruginous deposits, several cases have been observed in which deposits rich in manganoso-manganic oxide have been formed. Water from deep wells appears very frequently to be manganiferous; that from natural springs is generally free.

M. J. S.

Rivot's Quantitative Estimation of Iron in presence of Zirconium. ALEXANDER GUTBIER and C. TRENKER (*Zeit. anorg. Chem.*, 1903, 36, 302—312. Compare Abstr., 1902, ii, 701).—Polemical. A reply to Daniel and Leberle (Abstr., 1903, ii, 392).

A. McK.

Analysis of Ferrosilicon. HJ. LIDHOLM (*Zeit. angew. Chem.*, 1903, 16, 1030—1031).—About 0.3 gram of the finely powdered sample is fused in a nickel crucible with 15 times its weight of a mixture of 1 part of sodium potassium carbonate and 2 parts of sodium peroxide; this mixture should be perfectly dry. The mass is dissolved in water, acidified with hydrochloric acid in excess, and the silicic acid is separated as usual.

The process also answers for the estimation of sulphur, which may be precipitated with barium chloride after removing the iron with ammonia. In this case, some 10—15 grams of the sample should be operated on.

L. DE K.

Analysis of Commercial Nickel. AUGUSTE HOLLARD (*Ann. Chim. anal.*, 1903, 8, 401—405).—Five grams of the metal are dissolved in a large, narrow beaker, covered with a funnel, in 25 c.c. of

nitric acid and 25 c.c. of water, 10 c.c. of sulphuric acid are added, and the nitric acid is expelled by heating. The residue is dissolved in water, ammonia is added in slight excess, and the whole boiled for a moment. Twenty-five c.c. of ammonia are added, and then a few c.c. of hydrogen peroxide, and after diluting to 300 c.c. the nickel is precipitated as metal by electrolysis at 90° , using a current of 1 ampere. When all the nickel has deposited, the precipitate (of iron, &c., see later) is collected, redissolved in sulphuric acid, mixed with excess of ammonia, added to the main liquid, and the whole is once more submitted to electrolysis.

The nickel, which also contains any cobalt or copper, is, after weighing, dissolved in a mixture of 50 c.c. of nitric acid and 50 c.c. of water, and after diluting to 300 c.c. the copper is precipitated by means of a current of 1 ampere. The cobalt is separated from the nickel by the potassium nitrite process and finally deposited as metal by electrolysis.

The precipitate previously mentioned contains silica, alumina, iron, and also arsenic and antimony. After dissolving in dilute sulphuric acid, the arsenic and antimony are precipitated with hydrogen sulphide. After expelling the latter by boiling, 5 grams of citric acid and 25 c.c. of strong sulphurous acid are added, followed by 25 c.c. of ammonia. The liquid is now neutralised with dilute sulphuric acid, again made alkaline with a few c.c. of ammonia, diluted to 300 c.c., and electrolysed at 40° , using a current of 1 ampere. As the metallic iron so obtained is not pure enough for direct weighing, its exact amount is found by titration with permanganate.

The mother liquor from the iron is evaporated with sulphuric acid to destroy the citric acid, and in the resulting filtrate any aluminium, calcium, and magnesium are then estimated as usual.

Silicon and sulphur are estimated by treating 5 grams of the metal with nitric acid and expelling this by repeated evaporation to dryness with hydrochloric acid. The silica thus rendered insoluble is fused with sodium carbonate and potassium nitrate to obtain the remainder of the sulphur as sulphate, which, after being freed from silica by evaporation with hydrochloric acid, is then added to the main solution and precipitated with barium chloride. The silica is finally weighed and its purity ascertained by evaporation with hydrofluoric acid. Carbon is estimated as in steels. For the estimation of arsenic and antimony, compare the previous articles of the author (*Abstr.*, 1900, ii, 438, 442).

L. DE K.

Electrolytic Precipitation of Nickel from Phosphate Solutions. WALTER T. TAGGART (*J. Amer. Chem. Soc.*, 1903, 25, 1039—1041).—The nickel sulphate solution is precipitated with disodium hydrogen phosphate, the precipitate is redissolved in phosphoric acid, and the solution is then electrolysed in a platinum dish, serving as cathode, while a flat platinum spiral is used as anode. Some 40 experiments giving full details as to strength of currents, temperature, dilution, &c., are recorded, showing the accuracy of the method.

Attempts to separate in this manner nickel from manganese, iron, aluminium, and chromium were, however, unsuccessful. L. DE K.

Influence of Gases on the Separation of Metals by Electrolysis: Separation of Nickel and Zinc. AUGUSTE HOLLARD and L. BERTIAUX (*Compt. rend.*, 1903, 137, 853—855).—Hitherto it has been impossible to effect a separation of metals, the electrolytic potentials of which are higher than that of hydrogen; the difficulty is due to the evolution of hydrogen and oxygen at the cathode and anode, and the consequent increase in resistance of the cell. Suppression of hydrogen at the cathode (*Abstr.*, 1903, ii, 291) has led to the separation of zinc and cadmium; zinc and nickel can be separated by preventing the formation of oxygen at the anode. The evolution of oxygen can be avoided either by employing a soluble anode of zinc amalgam or by introducing sulphurous acid into the solution. The former method only permits the estimation of nickel; when both metals are to be determined, the latter process is adopted. The details are as follows: the cell is provided with platinum electrodes, the cathode being in the form of gauze. The solution occupies 300 c.c., and contains the nickel and zinc as sulphates, together with 10 grams of ammonium sulphate, 5 grams of magnesium sulphate, 5 c.c. of a saturated solution of sulphur dioxide, and 25 c.c. of aqueous ammonia of sp. gr. 0.924. Electrolysis is conducted at 90°, with a current of 0.1 ampere for four hours, after which a sample of the liquid should give no colour with ammonium sulphide. After passing the current for another hour, the process is complete and the deposit of nickel is weighed. S. S.

Separation of Chromium from Iron and Aluminium. GEORG VON KNORRE (*Zeit. angew. Chem.*, 1903, 16, 1097—1107).—Iron and aluminium may be completely removed from a solution containing chromium by adding an excess of pure ammonium persulphate and sufficient sulphuric acid to prevent the precipitation of basic ferric sulphate. On boiling the dilute solution, the chromium is converted into chromic acid, from which the iron and aluminium may be separated by means of ammonia. As the sesquioxides retain a trace of chromium, they should, after washing, be redissolved in dilute sulphuric acid and again boiled with persulphate. In accurate analysis, it is as well to repeat the operation a third time. The chromic acid may now be estimated in various ways, for instance, by acidifying the filtrate with sulphuric acid, diluting, and destroying the excess of persulphate by a 20 minutes' boiling, and finally titrating with ferrous sulphate and permanganate.

Iron may also be conveniently separated by the author's nitroso- β -naphthol process (*Abstr.*, 1887, 530) if to 100 c.c. of the liquid 5 c.c. of hydrochloric acid are added. The precipitate should be collected after remaining in a cold place for between 8 and 16 hours. If it is desired to estimate the chromium in the filtrate, this should be evaporated to dryness; the residue is then dissolved in dilute sulphuric acid, boiled with a little sodium hydrogen sulphite to reduce any chromic acid formed, and finally precipitated with ammonia. L. DE K.

Action of Hydrogen Peroxide on the Sulpho-salts of Tin, Antimony, and Arsenic. A. KOLB (*Zeit. angew. Chem.*, 1903, 16, 1034—1035).—A practical confirmation of the results obtained by Walker (*Trans.*, 1903, 83, 184). L. DE K.

Estimation of Titanium. J. WATSON BAIN (*J. Amer. Chem. Soc.*, 1903, 25, 1073—1091).—A criticism of the various methods for the separation of titanium. The most accurate process is that of Blair, fully described by Pope, for the particulars of which the reader is referred to the *Trans. Amer. Inst. Min. Eng.*, 29, 372.

Another excellent process is, however, that proposed by Baskerville (*J. Soc. Chem. Ind.*, 1900, 19, 419), which may be briefly summarised as follows. The ore is fused with potassium pyrosulphate, the fused mass is extracted with water, and the filtrate precipitated with ammonia, avoiding excess. The hydroxides are collected, washed, and redissolved in dilute hydrochloric acid. After neutralising as nearly as possible with ammonia, the liquid is saturated with sulphur dioxide and then boiled for three minutes. If the precipitated titanium dioxide is not perfectly white, the process must be repeated.

L. DE K.

Colorimetric Estimation of Bismuth. PAUL PLANÈS (*J. Pharm. Chim.*, 1903, [vi], 18, 385—389).—The method depends on the fact that, in the presence of glycerol, potassium iodide does not precipitate solutions of bismuth salts, but gives a yellow solution. Standard solutions are prepared by dissolving 1 gram of pure metallic bismuth in 3 c.c. of nitric acid and 2.8 c.c. of water and diluting the solution to 100 c.c. with glycerol. Five grams of potassium iodide are also dissolved in 5 c.c. of water and diluted to 100 c.c. with glycerol. Ten c.c. of each of these solutions, when mixed in a graduated tube and diluted to 50 c.c. with a mixture of glycerol and water, form the standard with which the comparisons are made. Sufficient of the bismuth salt to be estimated is taken to give an approximately 1 per cent. solution of bismuth when dissolved in nitric acid and made up with glycerol.

Conversely, the method serves for the estimation of iodides.

W. P. S.

Separation and Estimation of Iron and Phosphoric Acid in Water. HENRI CAUSSE (*Compt. rend.*, 1903, 137, 708—710).—Both iron and phosphoric acid are present in potable waters in the form of complex ions. The most suitable reagent is the compound of mercuric chloride with sodium *p*-aminobenzenesulphonate (*Abstr.*, 1900, ii, 457—458), which precipitates the iron as ferric hydroxide and the phosphoric acid as mercuric phosphate. After 24 to 36 hours, the clear liquid is decanted, and the precipitate is dissolved in hydrochloric acid, a residue of mercurous chloride remaining in the case of impure waters. The solution is evaporated to dryness and the residue fused with sodium carbonate. The iron and phosphoric acid are then separated in the usual way.

C. H. D.

Evaluation of Oil of Cloves. HERMANN THOMS (*Arch. Pharm.*, 1903, 241, 592—603).—The method of evaluation published by the author (*Ber. Deut. pharm. Ges.*, 1891, 1, 278; *Abstr.*, 1892, 250) has been examined in the light of subsequent publications. It is found that the original method accounts for most of the eugenol present as

acetate or benzoate; but a modification of the method is described which obviates any error due to the presence of eugenol esters. For rough estimations, the simpler method of Umney is permissible (*Pharm. J.*, 1895, 25, 950. Compare also Spurge, *ibid.*, 1903, Nos. 1717 and 1718).

In the modified method, about 5 grams of the oil are warmed with 20 grams of 15 per cent. aqueous sodium hydroxide for half an hour in a beaker on the water-bath; the mixture is then transferred to a separating funnel, the aqueous layer run off, and the residual oil washed twice with 5 c.c. of the sodium hydroxide. To the united alkaline liquid, in a beaker, 6 grams of benzoyl chloride are added; the whole is shaken, and then warmed to destroy the excess of benzoyl chloride. After cooling, the solidified benzoyl eugenol is filtered off and rinsed back into the beaker with 50 c.c. of water. The liquid is warmed until the crystals have melted together, and when the cake has become cold and solid again, the water is filtered off; this washing with 50 c.c. water is repeated twice more. Then 25 c.c. of 90 per cent. alcohol are added to the cake in the beaker, heat is applied until the solid has dissolved, and the beaker is swayed gently round for a few minutes as the contents cool, until the benzoyl eugenol has separated out in small crystals. The liquid is then cooled to 17° and filtered through a 9 cm. filter previously dried at 101° , the filtrate (about 20 c.c.) being collected in a graduated cylinder. The crystals are washed with so much more of the alcohol that the total filtrate amounts to 25 c.c., and then crystals and filter are brought into a weighing-glass, dried at 101° , and weighed. If a is the weight of benzoyl eugenol found, b the weight of oil of cloves taken, the total percentage of eugenol in the oil, as such and in the form of esters, is $61.2(a + 0.55)/b$, since 0.55 gram is the weight of benzoyl eugenol which dissolves in 25 c.c. of 90 per cent. alcohol at 17° .

If it is desired to estimate the free eugenol present, 5 grams of the oil are dissolved in 20 grams of ether, the solution shaken rapidly with 20, 5, and 5 grams in succession of 15 per cent. aqueous sodium hydroxide, and the united alkaline liquids treated with benzoyl chloride, &c., as in the other case.

A sample of the oil, distilled by the author from material which had been grown in the botanical garden at Victoria in the Cameroons, was found to contain 79.9 per cent. of eugenol, of which 9.0 was present in the form of esters. C. F. B.

Detection of Methyl Alcohol when Mixed with Ethyl Alcohol. LEONARD D. HAIGH (*Pharm. Rev.*, 1903, 21, 404—406).—Prescott's method (*Abstr.*, 1901, ii, 581), modified according to a suggestion by Mulliken and Scudder (*Abstr.*, 1901, ii, 43), was found to give trustworthy results. This modification consists in carefully boiling the liquid in the test-tube, after the treatment with the copper spiral, until the odour of acetaldehyde just disappears. The test for formaldehyde is then applied to the remaining solution. W. P. S.

Estimation of Methoxy- and Methylimino-groups. GUIDO GOLDSCHMIEDT and OTTO HÖNIGSCHMID (*Monatsh.*, 1903, 24, 707—719. Compare *Abstr.*, 1903, ii, 578; Busch, *Abstr.*, 1902, i, 501).—When

heated with hydriodic acid, the methylbetaines of quinolinic, pyridine-2:3:4-tricarboxylic, papaverinic, and pyropapaverinic acids, derivatives of pyridine containing the grouping $\cdot\text{CO}\cdot\text{C}\cdot\text{NMe}\cdot$, as also methylantranilic acid, yield part of the methyl attached to nitrogen, as methyl iodide, the more completely the greater the number of carboxyls present. Papaveraldine methiodide yields little if any of the *n*-methyl as methyl iodide (Decker, Abstr., 1903, ii, 763). Sarcosine, betaine, creatine, creatinine, and methylaminoacetophenone yield no methyl iodide with hydriodic acid. G. Y.

Estimation of Glycerol and the Methoxyl Group. MILAN J. STRITAR (*Zeit. anal. Chem.*, 1903, 42, 579—590).—A simple and compact apparatus is described for carrying out Zeisel's process (Abstr., 1902, ii, 111, 518), by which the use of tepid water in the condenser jacket can be dispensed with (compare Hewitt and Moore, Trans., 1902, 81, 318). A rapid method of collecting and drying the silver iodide is also described. In place of red phosphorus for the absorption of hydrogen iodide, a strong solution of sodium antimonyl tartrate has given good results. It also serves to indicate the presence of sulphur compounds, without, however, enabling the method to be used when sulphur is present. M. J. S.

Estimation of Glycerol in Wines by the Iodide Method. SIMON ZEISEL and RICHARD FANTO (*Zeit. anal. Chem.*, 1903, 42, 549—578. Compare Abstr., 1902, ii, 111, 585).—Wine is prepared for the estimation as follows: 100 c.c. are treated with a small excess of tannin and barium acetate and distilled (avoiding contact with caoutchouc) until 70 c.c. have passed over; the residue is made up to 50 c.c. (or 100 c.c. in the case of sweet wines), of which 5 c.c. are used for the estimation. Special experiments show that the alcohol and esters are completely removed, whilst no glycerol is lost. The method is inapplicable in its present form to wines in which any considerable quantity of mannitol is present. The influence of isobutylene glycol, which probably occurs as a normal constituent of wine in about the proportion of 7.5 to 100 of glycerol, has not yet been studied. Although sugar by itself yields small amounts of volatile iodides, which precipitate silver, it appears to cause a compensating loss in the glycerol estimation, so that the process is applicable to sweet wines. Experiments with the above process, side by side with Pasteur's alcohol-ether method, show that the loss of glycerol in the latter is so large, and the product is so impure, that no comparison can be made of wines analysed by the different methods. M. J. S.

Spontaneous Alteration of Fehling's Solution. LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1903, 241, 589—593).—If acid is added to Fehling's solution which has been kept for a time, a slight precipitate of cuprous oxide is formed before the alkalinity is all removed; this dissolves in excess of acid, but if excess of alkali is then added and the solution boiled it reappears. Such a solution contains tartaric acid; this must have resulted from the further oxidation of

dihydroxytartaric acid first formed, and in fact the behaviour of an old Fehling's solution is just like that of a fresh solution to which some sodium dihydroxytartrate has been added. Formic acid was also detected in solutions from $\frac{1}{4}$ — $\frac{1}{2}$ year old, but not in solutions 3 weeks and more than a year old respectively; oxalic acid could not be detected with certainty.

In practice, freshly mixed Fehling's solution should always be used if possible. If an old solution has to be added to an acid liquid, the latter should first be made alkaline, and the solution should be tested to see that it does not give a precipitate when merely boiled by itself.

C. F. B.

Quick Method for the Estimation of Sugar in Urine. EMIL C. BEHRENDT (*Ber.*, 1903, 36, 3390—3399).—The basis of the methods tried consists in adding a given volume of urine to a suitable solution and estimating the dextrose present by measuring the volume of the precipitate formed. The method does not give accurate results when the volume of cuprous oxide from Fehling's solution is measured, nor when the volume of mercury obtained from an alkaline solution of mercuric cyanide is measured. In both cases, the precipitates contain appreciable amounts of phosphates.

Better results are obtained when the following solution is employed: 32.747 grams of the basic nitrate, $\text{Bi}(\text{NO}_3)_2 \cdot \text{OH}$, $\text{Bi}(\text{OH})_2 \cdot \text{NO}_3$, dried at 105° , are mixed with 450 c.c. of 2*N* sodium hydroxide and 50 grams of Rochelle salt. Complete solution results and the whole is made up to a litre. Ten c.c. of this solution are mixed with 10 c.c. of diabetic urine in a graduated tube and boiled for $\frac{1}{2}$ to $\frac{3}{4}$ of an hour. The solution becomes darker in colour and ultimately deep black, and on cooling a precipitate of "bismuthous oxide" settles. A "precipitate saccharometer" has been constructed which is so graduated as to enable not merely the volume of the precipitate, but also the percentage of dextrose present, to be read off directly. Albuminous urines must be boiled, the precipitate filtered off, and the filtrate then examined. All urines containing more than 2 per cent. of sugar are diluted to double the volume before the estimation. The precipitate of "bismuthous oxide" always contains phosphates, but it has been shown that the amount is so small that it may be neglected.

The values obtained by the method either in urine or in aqueous solutions of dextrose are rather lower than those obtained by titration with Fehling's solution, but are sufficiently accurate for clinical purposes.

J. J. S.

Estimation of Raffinose. DAVID L. DAVOLL (*J. Amer. Chem. Soc.*, 1903, 25, 1019—1028).—The inverted acid solution, prepared according to Clerget's directions, is treated at 69° with powdered zinc. This effects an almost perfect decolorisation, and is preferable to the use of animal charcoal, as it does not cause a loss of raffinose.

L. DE K.

The Dextrins of Pine-Honey. OSCAR HAENLE and ALFRED SCHOLZ (*Zeit. Nahr. Genussm.*, 1903, 6, 1027—1031).—The so-called "honey-dextrins" found in pine-honey consist of various substances

which ferment with difficulty. They may be obtained by fermenting the honey with yeast. A part of these substances is insoluble in 87 per cent. alcohol, and may be precipitated from dilute alcoholic solution with barium hydroxide. The "honey-dextrins" reduce Fehling's solution to a small extent only, but, on inversion, about 30 per cent. of reducing carbohydrates are produced. They have a strong, right-handed polarisation (compare Abstr., 1902, ii, 180).
W. P. S.

Estimation of Starch in Yeast. NEUMANN WENDER (*Chem. Centr.* 1903, ii, 852—853; from *Verh. Deutsch. Naturf. Aertze*, 1902, ii, 96—98).—One or two grams of the suspected yeast are mixed in a graduated glass with 10 c.c. of water and 1 c.c. of iodine solution, and then transferred to a special tube. The glass is then rinsed with another 5 c.c. of water, and after adding this to the main portion the whole is whirled for 3 minutes in a special centrifugal apparatus styled "amylometer." The tubes are so graduated that the blue deposit represents at once the percentage of potato starch with 20 per cent. of water.
L. DE K.

New Quantitative Method. [Estimation of Wood-fibre in Paper.] NICOLAE TECLU (*Zeit. anal. Chem.*, 1903, 42, 603—606).—The sharply focused image of an object under the microscope loses distinctness as the distance of the objective from the object is altered, and at a definite distance the image disappears completely. This distance is, however, not the same for all objects, and in the microscopic examination of paper it is found possible to estimate the percentage of wood-fibre by measuring the distance at which the fibres, after staining red with phloroglucinol and hydrochloric acid, cease to be visible. For this purpose, the milled head of the fine adjustment is furnished with a scale, and the object on the stage is kept in motion by clockwork, as the accuracy of the measurement is much increased by observing the point at which the motion of the image can no longer be detected. An empirical constant must be determined for the optical combination in use.
M. J. S.

[Analysis of Fats.] ALFRED PARTHEIL and F. FÉRIÉ (*Arch. Pharm.*, 1903, 241, 545—569).—This vol., i, 4.

Estimation of Fat in Milk by Centrifugal Methods. J. VAN HAARST (*Milch.-Zeit.*, 1903, 32, 710—711. Compare Abstr., 1903, ii, 516).—The various centrifugal methods are compared. The Babcock-Lister process always gave too low results. Gerber's method, when properly performed, gave good results, as did also that of Thörner. Adam's process was used as a comparison.
W. P. S.

Detection of Heated Milk. MORITZ SIEGFELD (*Zeit. angew. Chem.*, 1903, 16, 962—963).—A controversy with Utz, chiefly on the employment of "ursol" and persulphates for the detection of milk which has been subjected to heating.
L. DE K.

Use of Phenolphthalin for the Detection of Heated Milk. FRANZ UTZ (*Milch.-Zeit.*, 1903, 32, 722).—The oxidation of phenolphthalin to phenolphthalein, previously described as a test for various
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ferments, including oxydase (compare Abstr., 1902, i, 514), cannot be used to distinguish between raw and heated milk. The reagent must be gently heated to obtain a coloration with raw milk, and under these conditions heated milk also gives a colour. W. P. S.

Poppy-seed Oil. FRANZ UTZ (*Chem. Zeit.*, 1903, 27, 1176—1177).—The test with nitric and sulphuric acids (1 : 1) does not properly distinguish between poppy-seed oil and sesamé oil. Nearly all commercial poppy-seed and sesamé oils are more or less mixtures, owing to the presses being used in turn for the extraction of these oils. Poppy-seed oil, extracted from the seed by light petroleum, gave the following iodine numbers (Hübl process): Indian, 153·48; Levantine, 157·52; German, 156·94, whereas supposed pure samples investigated by other authors gave about 137°. Tested in Zeiss's butyrefractometer, the pure oils showed respectively 78·1°, 78·4°, and 78·4°: sesamé oil showed 73°, and two commercial samples showed 76·7°. The pure oil also showed no polarisation whatever. L. DE K.

Estimation of Formaldehyde. BERNHARD H. SMITH (*J. Amer. Chem. Soc.*, 1903, 25, 1028—1035).—The author has tried the various recorded processes for the estimation of formaldehyde, and arrives at the conclusion that for dilute samples the only trustworthy methods are the iodometric and cyanide processes as proposed by Romijn (Abstr., 1897, ii, 166). For more concentrated solutions, the Blank and Filkenheimer hydrogen peroxide process, and also Legler's ammonia method, may be employed, but the gravimetric hexamethylenetetramine process and the volumetric aniline method are untrustworthy. L. DE K.

Estimation of Formaldehyde in Milk. BERNHARD H. SMITH (*J. Amer. Chem. Soc.*, 1903, 25, 1036—1038).—The author agrees with Leonard and Smith (Abstr., 1897, ii, 288) that addition of sulphuric acid accelerates the expulsion of formaldehyde from milk on boiling. If, however, an excess of acid is added, the distillation of the formaldehyde is much retarded.

The following process is recommended: 100 c.c. of milk are introduced into a 500 c.c. round bottomed flask, 1 c.c. of dilute sulphuric acid (1 : 3) is added, 20 c.c. of distillate are collected, and the formaldehyde is determined by the cyanide method (preceding abstract). If the sample is reasonably fresh, the amount found will be practically one-third of that existing in the sample. L. DE K.

***p*-Nitrophenylhydrazine as a Microchemical Reagent.** THEODOR H. BEHRENS (*Chem. Zeit.*, 1903, 27, 1105).—The hydrochloride of *p*-nitrophenylhydrazine is recommended as a microchemical reagent for all aldehydes and ketones, most of which yield characteristic crystalline precipitates. The reaction is of particular value for the microchemical determination of acetaldehyde, for which a trustworthy test was still wanting. This is obtained as orange-coloured needles, generally as stellate aggregates, but which may also occur isolated. To apply the test to glycerol, the concentrated liquid is heated in a tube with potassium hydrogen sulphate and a small piece of asbestos

to prevent frothing, and a drop of the condensed vapour is then mixed with the reagent (compare Abstr., 1901, ii, 351, and 1903, ii, 246, 455).
L. DE K.

Phosphomolybdic Acid, a Characteristic Reagent for the Amino-group. FREDERIC SEILER and A. VERDA (*Chem. Zeit.*, 1903, 27, 1121—1125).—A lengthy article containing a table showing the action of phosphomolybdic acid on the various amino-derivatives.

The reduction of the reagent caused by some oils and fats must be attributed to the presence of amino-compounds in them. L. DE K.

Iodometric Estimation of Benzidine and Tolidine. ARMAND ROESLER and BORIS GLASMANN (*Chem. Zeit.*, 1903, 27, 986).—About 5 grams of the base are dissolved in hot water with the addition of 5 c.c. of hydrochloric acid and when cold diluted to 500 c.c. Twenty-five c.c. of this solution are neutralised with solution of sodium hydrogen carbonate until a slight precipitate forms, which is then redissolved by means of a drop of very dilute hydrochloric acid. The liquid is now diluted to 500 c.c. and *N*/20 iodine is then slowly added while stirring until no further precipitate is produced and a drop of the supernatant liquid gives a blue spot on starch-paper: 254 parts of iodine represent 184 parts of benzidine or 211.6 parts of tolidine.
L. DE K.

Identification of Alkaloids. P. KLEY (*Rec. trav. chim.*, 1903, 22, 367—384).—The author proposes to apply a slightly modified form of the microscopic method of determining the refractive index of crystals, by immersion in an indifferent liquid of known refractive index, to the detection of alkaloids, especially in toxicological work. The refractive indices of a number of suitable liquids and those of the crystals of a large number of the common alkaloids are given in the original. From the results, the author deduces the conclusion that certain commercial brands of various alkaloids are not homogeneous.
T. A. H.

Comparison of Chemical and Physiological Methods of Assaying Aconite. A. B. STEVENS (*Pharm. Arch.*, 1903, 6, 49—55).—Ten grams of aconite root are macerated for four hours in 75 c.c. of a mixture of alcohol (7 vols.) with water (3 vols.) and then percolated with the same solvent until 150 c.c. of solution are obtained. This, mixed with 5 grams of powdered pumice stone, is evaporated on a dinner plate heated by a water-bath, and the residue dissolved as far as possible in 5 c.c. of *N*/10 sulphuric acid diluted with 10 c.c. of water, the insoluble matter being washed with 40 c.c. of water. The filtrate is made alkaline by the addition of 2 c.c. of ammonia solution and the liberated alkaloid extracted with ether. The residue left after distilling off the ether is dissolved in 3 c.c. of *N*/10 sulphuric acid and the solution titrated with *N*/50 alkali, using hæmatoxylin as an indicator. Similar methods are described for the assay of aconite preparations, and these are stated to give trustworthy results except in the case of extracts which have been heated in the course of preparation. Results of the same order are obtained by determination of the dilution neces-

sary to inhibit the causation of a tingling sensation when a drop of an aconite preparation is applied to the tip of the tongue (Squibb's test), and by observation of the toxicity of aconite preparations towards frogs, but owing to the variation in sensibility of frogs, this physiological test is untrustworthy.

T. A. H.

Assay of Crude Cocaine. WILLIAM GARSEED (*Pharm. J.*, 1903, [iv], 17, 784—791).—An account is given of a large number of experiments carried out with the object of devising a method for assaying the crude alkaloid obtained from different kinds of coca leaves. A comparison was made of the chemical and physical properties of the four alkaloids, cocaine, cinnamylcocaine, truxilline, and tropacocaine, and of their hydrolytic products, namely, benzoic, cinnamic, and truxillic acids. As a result of these experiments, it was found that the proportions of the different alkaloids present in the crude material may be ascertained by either of the following processes.

In the first process, a weighed quantity of the crude alkaloid is dissolved in dilute sulphuric acid and treated with potassium permanganate. The cinnamylcocaine is thus destroyed, whilst the cocaine and truxilline remain unaffected and are recovered by adding excess of ammonia and extracting with ether. The unoxidised alkaloid is weighed, and the loss in weight represents the amount of cinnamylcocaine originally present. The re-extracted alkaloid is hydrolysed by heating it with alcoholic potassium hydroxide, and the truxillic and benzoic acids are separated from one another by taking advantage of the insolubility of the former in water. From the quantity of each acid found, the respective amounts of truxilline and cocaine can be calculated.

In the alternative process, the crude alkaloid is submitted to alkaline hydrolysis. The cinnamic acid is estimated by acidifying the product with sulphuric acid and adding excess of solution of bromine, $2\frac{1}{2}$ mols. of bromine being absorbed by each molecule of cinnamic acid. The excess of bromine is removed by means of potassium iodide, and the liberated iodine is titrated with sodium thiosulphate. The benzoic and truxillic acids are not affected by this treatment and are separated from one another by means of the insolubility of the latter in water. The amounts of truxilline and cinnamylcocaine are then calculated, and the quantity of cocaine in the crude alkaloid is found by difference.

The first process is preferable to the second, since in the former case the amount of cocaine present is ascertained by direct estimation of the benzoic acid, whilst in the latter it is determined by difference.

E. G.

Test for Choline in Blood. RICHARD W. ALLEN and HERBERT FRENCH (*Proc. physiol. Soc.*, 1903, xxix—xxx; *J. Physiol.*, 30).—The mere obtaining of yellow, octahedral crystals by the addition of platinum chloride to an alcoholic extract of blood is by itself no proof of the existence of choline. Ammonium and potassium platinichlorides have a similar crystalline form, and the use of absolute alcohol does not exclude these in small amounts. In order that the test may be of

clinical value, some solvent must be discovered which excludes ammonium and potassium salts. W. D. H.

Xanthine Bases contained in Meat, Yeast, and other Extracts. I. The Xanthine Bases of Meat Extract. KARL MICKO (*Zeit. Nahr.-Genussm.*, 1903, 6, 781—791).—The present researches were undertaken for the purpose of separating the xanthine bases in meat extract from one another, and further to ascertain whether the same bases occur in meat and vegetable extracts. For the extraction of the total mixed bases, the method previously described by the author was used (compare Abstr., 1902, ii, 369). The bases were then decolorised by heating with lead acetate solution and adding ammonia. After removing the excess of lead, the bases were fractionally crystallised, the different fractions being further purified by the lead and ammonia treatment, and then analysed. From the results, it is seen that the xanthine bases of meat extract consist principally of hypoxanthine, xanthine itself being present only in small quantity. Adenine was also found in the last fraction mixed with hypoxanthine, and was separated from the latter by precipitation with picric acid, dissolving the precipitate in hydrochloric acid, and removing the picric acid by extraction with toluene. The bases were then precipitated with ammoniacal silver solution, the free base being obtained from the silver salt, purified by the lead treatment, and recrystallised from water. Carnine and guanine were not detected in meat extract.

W. P. S.

Two Colour Reactions of Yohimbine. G. MEILLERE (*J. Pharm. Chim.*, 1903, [vi], 18, 385).—A crystal of the alkaloid is heated in a porcelain basin on a water-bath with a few drops of dilute sulphuric acid (1 : 1) and a trace of sucrose, dextrose, or furfuraldehyde. When a red coloration appears, the basin is removed from the water-bath and its contents cooled. On spectroscopic examination, a large absorption band is seen in the blue part of the spectrum.

A burnt-sienna coloration is obtained by evaporating a solution of the alkaloid in concentrated nitric acid, and treating the residue with ammonia. W. P. S.

Reactions of Methyl-violet and Tropæolin. SCHUMACHER-KOPP (*Chem. Zeit.*, 1903, 27, 1176).—As there seems to be a little confusion as to the behaviour of these indicators towards acids, the author has reinvestigated the matter. Methyl-violet turns green or blue in the presence of hydrochloric, sulphuric, nitric, or phosphoric acid. Boric acid gives no reaction. Of the organic acids, oxalic, tartaric, and lactic acid give a bluish-green coloration: citric acid gives a blue, and acetic acid is quite indifferent.

Tropæolin behaves similarly. Hydrochloric, sulphuric, nitric, and phosphoric acids give a reddish-violet coloration, boric acid gives no reaction. Oxalic and tartaric acids also give this reaction, whilst citric acid gives a yellowish-red, lactic acid a rose, and acetic acid a cherry-red coloration. L. DE K.

Reaction for Fruit Tannin and other Tannins. W. KELHOFER (*Chem. Centr.*, 1903, ii, 1090—1091; from *Schweiz. Woch. Pharm.*, 41, 457—461).—When a drop of fruit or grape wine is boiled with 10 c.c. of concentrated hydrochloric acid or sulphuric acid, the tannin present in the wine yields a violet coloration. Oak- and kino-tannin also give this reaction, but the tannic acids contained in gall apples, moringa, or coffee do not. The coloration is not obtained when formaldehyde is present, and aliphatic aldehydes more or less affect its formation. The colouring matter is dissolved by ether, forming a reddish-violet solution, but the substance appears to be stable only when dissolved in concentrated acid. Sulphur dioxide and plant acids have no effect on the reaction. The coloration may possibly serve as a basis for a colorimetric method of estimating the tannin in wine. A violet coloration, which probably also depends on the presence of tannin, is formed when freshly cut sections of young pears are treated with fuming hydrochloric acid at the ordinary temperature. E. W. W.

Estimation of Indican in Urine. JACOB BOUMA (*Zeit. physiol. Chem.*, 1903, 39, 356—374).—A critical examination of the methods adopted for the estimation of indigo compounds in urine. The recent work of Maillard (*Abstr.*, 1903, ii, 563) is considered to confirm the author's views. W. D. H.

Estimation of Indican in Urine. L. MONFET (*Compt. rend. Soc. Biol.*, 1903, 55, 1251—1252).—One hundred c.c. of urine, 100 c.c. of hydrochloric acid, and 50 c.c. of hydrogen peroxide are warmed to 50° and shaken with 40 or 50 c.c. of chloroform. The chloroform extract is evaporated, boiled with 10 per cent. nitric acid, and rendered alkaline with potassium carbonate. The phenol so formed is estimated colorimetrically with potassium picrate; 100 parts of phenol is equivalent to 140 of indigotin. W. D. H.

Improved Method for Estimating Indigotin with Sodium Hyposulphite. ARTHUR BINZ and AUGUST KUFFERATH (*Chem. Centr.*, 1903, ii, 398; from *Färberzeit.*, 14, 225—226).—The hyposulphite solution is contained in a burette fitted with a three-way cock, and is delivered through a capillary tube passing through one of the holes of a doubly-bored rubber stopper placed in the neck of a distilling flask of 180 c.c. capacity containing 100 c.c. of the solution of indigotinsulphonic acid to be titrated; through the second hole passes a capillary tube reaching to the bottom of the flask, which allows a current of hydrogen gas to be passed through the solution. The contents of the burette and the solution of hyposulphite are kept in an atmosphere of hydrogen, and a layer of benzene covers the solution in the flask. To carry out an analysis, the burette is filled and the solution allowed to run out through the three-way tap, so that none of it passes into the flask; hydrogen at the same time enters, and in this manner all oxygen is removed from the sides of the burette. Hydrogen is then bubbled through the solution in the flask, and after exhausting with a pump for 5—10 minutes so as to remove traces of oxygen, the titration is carried out in the usual manner.

It is pointed out that, if sulphonation of the indigotin is carried out at 45°, different values are obtained from those which are given by samples sulphonated at 55°, but between 53° and 65° constant numbers are obtained.

W. A. D.

Detection of Urobilin. WILHELM SCHLESINGER (*Chem. Centr.*, 1903, ii, 855—856; from *Deutsch. Med. Wochschr.*, 29, 561—563).—In order to obtain a proper reaction for urobilin in urines, it is recommended to clarify them first by adding an equal volume of a 10 per cent. solution of zinc acetate in absolute alcohol; the filtrate will then show a fine fluorescence and distinct absorption spectrum. Zinc chloride should not be substituted for the acetate, and if an aqueous solution of zinc acetate is used the test is interfered with owing to oxidation taking place. If much bilirubin is present, this should be first removed. Fæces are first extracted with ether, then with acidified alcohol, and, after neutralising the acid with ammonia, an equal bulk of the alcoholic zinc solution is added. Blood may be also tested after first removing the blood corpuscles as usual by adding sodium chloride and potassium oxalate and centrifugalising the liquid. The clear plasma is then mixed with the zinc solution and again centrifugalised.

L. DE K.

Estimation of Bile Salts in Urine. OTTO GRUNBAUM (*Proc. physiol. Soc.*, 1903, xxvi—xxvii; *J. Physiol.*, 30).—The principle of the method depends on the fact that the addition of bile salts to urine accelerates the flow of the urine in drops through a small orifice. A specially constructed pipette for counting the drops in a given time is described.

W. D. H.

Colour Reactions of Proteids. SYDNEY W. COLE (*J. Physiol.*, 1903, 30, 311—318).—Liebermann's test is due to an interaction between glyoxylic acid contained in the ether used in washing the proteid and the tryptophan split off from the proteid by hydrochloric acid. The acid in the ether arises by oxidation through the stage of vinyl alcohol and its isomeride acetaldehyde. The oxidation is effected in sunlight, primarily by the atmospheric oxygen and secondarily by the hydrogen peroxide produced in this way.

Proteids give an intense purple coloration when heated with strong hydrochloric acid and a little cane-sugar or furfuraldehyde, the reaction being due to tryptophan. Sometimes the reaction occurs with hydrochloric or sulphuric acid alone, the furfuraldehyde in this case being formed from the proteid itself. Reichl showed that proteids give a blue coloration when heated with hydrochloric acid, ferric chloride, and benzaldehyde. This is also due to tryptophan.

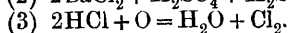
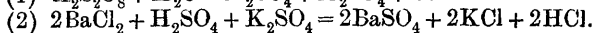
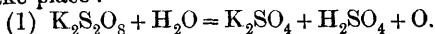
W. D. H.

Detection of Albumin in Urines. EMILE DUFAU (*J. Pharm. Chim.*, 1903, [vi], 18, 253—256).—Attention is called to the fact that many urines contain substances which share most of the reactions of true albumin, but are distinguished from it by not being coagulated on boiling the urine and by not giving a decided ring when

applying the Heller, or nitric acid test. They are, however, precipitated by addition of acetic and other acids, even partially in the cold, and thus lead to erroneous conclusions. L. DE K.

Moser's Blood Crystals. WALTHER FRIEBOES (*Pflüger's Archiv*, 1903, 98, 434—451).—Moser's method of obtaining crystals of oxy-hæmoglobin consists in allowing the defibrinated blood to become nearly dry, adding water, and waiting for crystals to appear. He states that the crystals so obtained from human blood are different in form from those of other animals, and can be employed for distinguishing human from other blood. In the present research, it was found that crystals prepared from human blood are different in form if the blood is removed during life or after death, different when the amount of blood used is large or small; further differences were found in the blood removed from the splenic vein, and from the umbilical cord of the new-born infant. Such differences show that it is impossible to employ these crystals for diagnostic purposes; moreover, dried or decomposed blood does not give them. A large number of photo-micrographs accompany the article; those of human and other bloods show rhombic plates, needles of varying sizes and groupings, but no essential crystallographic differences. W. D. H.

Van Deen's Reaction for Blood Spots. DIOSCORIDE VITALI (*Gazzetta*, 1903, 33, i, 323—328).—The author has confirmed experimentally the result obtained by Tarugi (Abstr., 1903, ii, 460) that van Deen's reaction is yielded by thiocyanates as well as by the colouring matter of the blood. It must also be assumed that the action of ozonised turpentine oil on thiocyanates yields either Caro's acid or a similar unstable compound, and the author finds that, on heating potassium persulphate with barium chloride, the following reactions take place:



In the reaction between potassium thiocyanate, barium chloride, and turpentine oil, however, it has been found impossible to detect the evolution of chlorine, possibly owing to its extremely small amount.

The author does not agree with Tarugi in the opinion that the value of van Deen's reaction for detecting blood is diminished by the fact that it is given also by thiocyanates. For, on the one hand, the latter are never found, except in infinitesimal amount, in blood spots (even when these are formed) of the residue from the evaporation of the urine or saliva, and, on the other, if the thiocyanate is present in larger quantity it can be detected readily by its reaction with ferric salts. T. H. P.

General and Physical Chemistry.

Budde Effect with Reference to Bromine. B. PALMER CALDWELL (*Amer. Chem. J.*, 1904, 31, 61—63).—Comparative experiments on the Budde effect in the cases of chlorine and bromine were carried out with the aid of photographic flash-light cartridges. These experiments were of a preliminary nature, and the gases were not perfectly pure or dry. The results showed that the expansion of the bromine was considerably greater than that of the chlorine. The return to the original volume was not immediate, but, on an average, extended through a period of 3 seconds. The rise in temperature was not sufficient to account for the change in volume, especially in the case of bromine. These results confirm the conclusion of Mellor (*Trans.*, 1902, 81, 1291) that there is no evidence to show that chlorine gas under the influence of light undergoes any change capable of appreciably affecting its activity towards hydrogen, and also indicate that the same is true in the case of bromine. If Mellor's second conclusion that the Budde effect is entirely caused by part of the energy absorbed from light being dissipated as heat were true, the rise of temperature should be much greater in the case of bromine than of chlorine, but this is not in accord with the results of the present investigation.

E. G.

Behaviour of Selenium towards Light and Temperature. ROBERT MARC (*Zeit. anorg. Chem.*, 1903, 37, 459—474).—The applicability of selenium cells for spectrophotometric purposes has been investigated. The course of the action of red and blue light on the cell used is gradual, the maximum influence being attained after from 6 to 7 hours.

The "non-metallic" variety of selenium, the resistance of which increases with increase of temperature, is termed by the author the A modification, whilst the "metallic" variety is termed the B modification. The latter is in general a much better conductor, and is less sensitive to light than the former. When the modification B is heated above 210°, it is transformed into A; when the latter is cooled to -40°, it is transformed into B. B is stable under 8°, A above 70°. At the ordinary temperature, A passes slowly into B, a transformation which is accelerated by white or red light but retarded by blue. The sensibility of selenium towards red and blue light at different temperatures is represented diagrammatically.

The author is of the opinion that the sensibility of selenium to light is not conditioned by the presence of traces of metallic impurities.

A. McK.

Characteristics of Line and Band Spectra. Origin of the Two Spectra. HENRI DESLANDRES (*Compt. rend.*, 1903, 137, 1013—1018).—The paper is largely an historical survey of the

theories advanced in explanation of the line and band spectra of elements. Adopting the Lorenz theory that the electric current is due to the movement of electrons, the author suggests (1) that the general band spectra arise from the impact of the electrons on the molecules of the gas, (2) the simpler band spectra (those of the negative pole) are to be attributed to the decomposition of the molecule into simpler molecules or even atoms, and (3) the line spectra are caused by a new series of vibrations arising from the union of the negative electrons with the atoms.

M. A. W.

Relation between the Constitution and Absorption Spectra of Rosaniline Dyes. JULIUS FORMÁNEK (*Zeit. Farb. Text. Chem.*, 1903, 2, 473—482).—Derivatives of *p*-diaminotriphenylmethane (malachite-green, brilliant-green, acid-green, patent-blue) give in concentrated solution in all solvents the same absorption spectrum, consisting of a double band with a slight shadow to the right (more refrangible side); in dilute solution, the double band reduces to a weak symmetrical single band. Derivatives of *p*-triaminotriphenylmethane similarly give a spectrum consisting in concentrated solution of a strong double band and a single weak line, and in dilute solution of two single bands, one much feebler than the other. In the latter case, the feeble band may be either to the right or the left of the principal line, according to the nature of the compound.

By introducing successive ethyl radicles into diaminotriphenylcarbinol chloride, the single band of dilute solutions is displaced in the direction of greater wave-length; di-, tri-, and tetra-ethyldiaminodiphenylcarbinol have, for instance, $\lambda = 561.4, 589.8, \text{ and } 623.0$ respectively. Similar displacement takes place in passing from di- to tetra- and hexa-methyltriaminotriphenylcarbinol anhydrochlorides, and the feebler band undergoes also a change in position in the same direction. It is shown that in both diamino- and triamino-triphenylcarbinol dyes the displacement in passing from the unalkylated base to alkylated derivatives is numerically proportional to the number of alkyl groups introduced. Thus the ratio

displacement in passing from base to dimethyl derivative

displacement in passing from same base to tetramethyl derivative
is equal to the same ratio in the case of the diethyl and tetraethyl bases; in the first case, the ratio is 0.4604, in the other, 0.4610. Whence, knowing the position of the bands of the methyl derivatives of a base, that of the ethyl derivatives may be calculated; examples are given, showing that the calculated values agree with those observed within half a wave-length.

In similar compounds, a chlorine atom produces exactly the same proportional displacement of the principal absorption band. In the case of triaminotriphenylcarbinol compounds, the distance between the intense and feeble bands diminishes as the index of refraction of the solvent increases. By comparing the displacement in passing from triaminotriphenylcarbinol anhydrochloride to tetramethylpararosaniline chloride, $\text{NMe}_2\text{Cl}:\text{C}_6\text{H}_4:\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, and to benzoyltetramethylpararosaniline chloride,

$\text{NMe}_2\text{Cl}:\text{C}_6\text{H}_4:\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)\cdot\text{C}_6\text{H}_4\cdot\text{NHBz}$,

it is seen that the change of position of the strong line is the same in both cases, but that of the weak line different; the values are λ 584.5 and λ 584.5 for the strong line, λ 527.6, λ 514.4 for the weak one. The weak band is thus affected only by changes in the third amino-radicle; by displacing both its hydrogen atoms by benzyl groups its intensity is much increased. The displacement of this band by a benzyl group is, however, much less than that caused by a methyl radicle. The remainder of the paper deals with the effects on the position of the lesser band caused by the radicles benzyl and phenyl being introduced in place of the hydrogen atoms of the third amino-radicle, and the use to which the numerical values obtained can be put in checking the structure of dyes. W. A. D.

Ultra-violet Absorption Spectra of Ortho-, Meta- and Para-isomerides. II. R. MAGINI (*Atti R. Accad. Lincei*, 1903, [v], 12, ii, 260—267. Compare Abstr., 1903, ii, 706).—From the results of his former experiments (*loc. cit.*) and of those now described on the ultra-violet absorption spectra of the isomeric aminobenzoic and phthalic acids, the author draws the following conclusions: (1) all the compounds examined exhibit very strong absorptions. (2) They nearly always show distinct bands, which become displaced towards the luminous part of the spectrum when a hydroxyl group is replaced by either a carboxyl or an amino-group. (3) The introduction of a second carboxyl group into the chain seems to annul completely the increase of absorption and displacement of the bands produced by the first. (4) As regards increase of absorption, especially that exhibited for very high dilutions in the extreme ultra-violet, the isomerides examined always arrange themselves in the order meta, ortho, para. (5) The meta- and ortho-isomerides show, although different, yet analogous absorptions, whilst the corresponding para-compounds exhibit extremely intense absorptions, quite independent of those of the other isomerides.

Hence it is clear that the positions of the groups constituting a molecule have a definite characteristic influence on the absorption of the ultra-violet rays. This influence, manifested in a particular way on the rays of small wave-length, shows that the absorption of a compound cannot be an additive property, as Spring's results for the visible part of the spectrum would indicate. T. H. P.

Ultra-violet Rays and Stereo-chemical Isomerism. R. MAGINI (*Atti R. Accad. Lincei*, 1903, [v], 12, ii, 297—304. See preceding abstract).—From measurements on the absorption spectra of asparagine, the tartaric acids, and maleic and fumaric acids, the author concludes: (1) that stereo-chemical isomerides which exhibit complete concordance in all their properties, with the exception of the rotatory power, which may be different, have, at least, in the compounds examined, perfectly identical absorptions, conditioned by the equality of their molecular dimensions. (2) That stereo-chemical isomerides containing a double linking determining *cis*- and *trans*-modifications, as in maleic and fumaric acids, show, on the other hand, absorptions which are markedly different, but of the same order of magnitude, this behaviour

being conditioned by the different configurations of the respective molecules. T. H. P.

Action of Ultra-violet Light on Rare Earth Oxides. CHARLES BASKERVILLE (*Amer. J. Sci.*, 1903, [iv], 16, 465—466).—The oxides of gadolinium, lanthanum, neodymium, praseodymium, cerium, samarium, thorium, yttrium, erbium, uranium, ytterbium, titanium, and zirconium were subjected to the action of ultra-violet light. Zirconium and thorium dioxides were the only two which phosphoresced strongly. Various minerals, containing zirconium and thorium, were also examined, but none of them showed any fluorescence or phosphorescence. A. McK.

Calculation of the Electromotive Force between Elements of the Calomel Element Type. J. N. BRONSTED (*Zeit. anorg. Chem.*, 1903, 37, 158—163).—The electromotive force of an element of the calomel element type is expressed by the equation $\pi = \nu(1/n_1 + 1/n_2)RT/\epsilon_0 \cdot \log p_1/p$, where ν is the number of metal atoms contained in 1 molecule of the salt, n the valency of the cation, and n_2 the valency of the anion. A. McK.

Electric Osmose in Liquid Ammonia. MARCEL ASCOLI (*Compt. rend.*, 1903, 137, 1252—1255).—When a difference of potential is established between two portions of liquid ammonia separated by a porous septum of calcined alumina, and kept at a temperature of -60° by immersion in a bath of acetone cooled with solid carbon dioxide (compare Moissan, *Abstr.*, 1902, ii, 66), there is usually a slight displacement of the liquid in the opposite direction to the current; but if the liquid is coloured blue by the formation of a small quantity of sodammonium in solution (compare Joannis, *Abstr.*, 1890, 209), there is a marked displacement of the liquid in the same direction as the current, showing that the introduction of the sodium has caused the liquid to become positively and the alumina negatively electrified (compare Perrin, *Compt. rend.*, 1903, 136, 1388—1391, 1441—1443; this vol., ii, 8). That liquid ammonia should exhibit the phenomenon of electric osmose is in keeping with its high dielectric constant (compare Goodwin and Kay Thompson, *Phys. Rev.*, 1899, viii, 38) and its ionising property (compare Frenzel, *Abstr.*, 1900, ii, 474). M. A. W.

Heat of Oxidation of Molybdenum. MARCEL DELÉPINE (*Bull. Soc. chim.*, 1903, [iii], 29, 1166—1167).—This constant was determined by the method already described (Delépine and Hallopeau, *Abstr.*, 1900, ii, 8). One gram of molybdenum, when burned to the trioxide, developed in a first experiment 1740.7 cal., and in a second, 1720.6 cal.; whence $\text{Mo(sol)} + \text{O}_3(\text{gas}) = \text{MoO}_3(\text{sol}) + 166.14 \text{ Cal. at constant volume, and } 167 \text{ Cal. at constant pressure.}$

Molybdenum dioxide burns very slowly to the trioxide, hence it is impossible to determine the calorific value of this reaction.

The heat of formation of molybdenum trioxide is less than that of tungsten trioxide (*loc. cit.*), and this agrees with the observed re

actions of the two metals. Thus the oxides of bismuth, antimony, lead, and copper are reduced by molybdenum, and molybdenum oxide is reduced by zinc, but less easily than tungsten oxide, whilst it also accounts for the limited reduction of molybdenum oxides by hydrogen as observed by Guichard (Abstr., 1900, ii, 658). T. A. H.

The Possible Forms of the Melting Point Curve for Binary Mixtures of Isomorphous Substances. II. JOHANNES J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 244—259. Compare Abstr., 1903, ii, 631).—A mathematical paper unsuitable for abstraction. A. McK.

Distillation under Diminished Pressure in Quartz Vessels. ALOIS SCHULLER (*Zeit. anorg. Chem.*, 1903, 37, 69—74).—Various substances were heated under diminished pressure in vessels of quartz, 22 cm. long and 2 cm. in diameter. It was shown that silver can be volatilised at a temperature below its melting point; a deposit of lead was observed when commercial silver was employed. Copper can be sublimed when heated in quartz vessels. Gold volatilises very slowly at about its melting point. Tin can be distilled somewhat more easily than gold.

Sodium chloride is readily sublimed. Silver sulphide is more readily sublimed than silver. Lead sulphide is very easily sublimed.

The author separated metals by distillation under diminished pressure before Kahlbaum, Roth, and Siedler (Abstr., 1902, ii, 259) did. A. McK.

The Influence of Non-electrolytes on the Vapour Tension of Acetic Acid in Solution. PETRU BOGDAN (*Ann. sci. Univ. Jassy*, 1903, 11, 302—327).—A description of some experiments which were made to ascertain the nature of the influence exerted by different compounds on the vapour pressure of a substance in solution. The actual case studied was that of acetic acid dissolved in benzene. The method employed was to maintain equilibrium between the benzene solution and aqueous acetic acid, and to determine the change in concentration of the latter produced by adding a second substance to the benzene layer. To compare the action of different substances, it is necessary to calculate the relative molecular depression in each case. This value was found to vary considerably; it is very small for toluene and ethylene dibromide, slightly larger for nitrobenzene and chloroform, and of considerable magnitude in the case of ether and the esters of acetic acid. Within certain limits, the molecular depression of each substance is constant; it is only slightly influenced by temperature, but increases with diminishing concentration of acetic acid until a point is reached when it remains constant, whatever the strength of the acetic acid solution.

A theoretical discussion is given of the two general cases (*a*) where the added substance depresses, or (*b*) raises the vapour pressure of the compounding solution. In the former case, it is shown that the two substances contained in the solution must be more soluble in one another than in the solvent, whilst in the second case the reverse

holds; the two dissolved substances are less soluble in one another than in the solvent. S. S.

Theory of the Critical State. Difference between Gasogenic and Liquidogenic Substances. ISIDOR TRAUBE (*Zeit. anorg. Chem.*, 1903, 37, 225—242. Compare Abstr., 1902, ii, 551).—According to the views of de Heen and of the author, the critical temperature is that at which the complete miscibility of two heterogeneous substances occurs; according to de Heen, those two substances differ from one another in their mass, and, according to the author, in the different space they occupy. The author's hypothesis, which implies a discontinuity of the gaseous and liquid state at the critical temperature, is supported by facts which are quite independent of critical phenomena. In the transformation of a solid and liquid substance into the gaseous form, the value b in van der Waal's equation must undergo a discontinuous and very considerable increase in volume, since the gasogenic particle is considerably greater than the liquidogenic particle. The "true" critical temperature is that temperature at which the densities of the gasogenic and liquidogenic particles are identical.

The co-volume, $v - b$, is a function of the pressure and the temperature; the constant b is a function of the pressure, either external or internal; the refraction constant, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}$, is likewise dependent on the pressure, but to a less extent than b .

A. McK.

Extension of Clapeyron's Formula to all the Indifferent States. L. ARIES (*Compt. rend.*, 1903, 137, 1239—1242. Compare Abstr., 1903, ii, 589; this vol., ii, 16).—From mathematical considerations, the author deduces the relation $\delta p / \delta T = \Delta S / \Delta V = \Delta L / T \Delta V$, where ΔS and ΔV denote the variations in entropy and volume, ΔL the latent heat of transformation absorbed by the system, and δp and δT the changes in pressure and temperature. This is Clapeyron's formula generalised, applicable to all the indifferent states, and proves that these states succeed one another in a determined direction if the temperature and pressure in a univariant system, and also the quantities of the constituents in a bivariant system, begin to change; the relation between the temperature and pressure can be expressed in curve form, and in the case of a system defined by means of its independent constituents every curve of a univariant state is met tangentially by the curves of the bivariant states.

M. A. W.

A New Heating Oven for Sealed Tubes, which can be Shaken. HERMANN THOMS (*Ber.*, 1903, 36, 3957—3958).—The apparatus described and depicted is heated by gas and has the form of an ordinary Carius-oven; it is mounted on trunnions on which it rocks, the movement being produced by a hot air or 1/40 h.p. electric motor. The temperature can be kept constant within 1—2°.

W. A. D

Ionisation in Atmospheric Air. J. A. McCLELLAND (*Sci. Trans. Roy. Dubl. Soc.*, 1903, 8, ii, 57—64. Compare Wilson, Abstr., 1901, ii, 435; Rutherford and Allen, Abstr., 1903, ii, 123).—The author has determined the number of ions present in 1 c.c. of air circulating freely through the apparatus. The number found was of the order 600—700, but there is very considerable variation in the amount of the ionisation. The maximum ionisation observed was about 2.5 times the minimum ionisation observed, the greatest value being obtained after several hours' rain. The radiation emitted by freshly fallen rain (Wilson, Abstr., 1903, ii, 194) is probably responsible for this. The facts, on the whole, point to some radioactive substance disseminated through the atmosphere. J. C. P.

Determination of the Nature of the Dissociation of Ternary Electrolytes by means of Isohydric Solutions. GOTTFRIED KÜMMELL (*Zeit. Elektrochem.*, 1903, 9, 975—977).—In a solution of magnesium chloride, we must assume the presence of the ions MgCl' , Mg'' , and Cl' in addition to undissociated molecules. The concentration of the Cl' ions can be determined by finding a solution of potassium chloride, for example, of such concentration that when it is mixed with the solution of magnesium chloride the conductivity of the mixture is the mean of the conductivities of the components. The concentrations of the Cl' ions in the two solutions are then the same. The following values are found in this way:

| | | | | | | |
|------------------------------------|-------|-------|-------|-------|--------|--------|
| Gram eq. MgCl_2 per litre | 2 | 1.5 | 1 | 0.5 | 0.1 | 0.05 |
| Gram eq. Cl' per litre | 1.133 | 0.872 | 0.593 | 0.310 | 0.0722 | 0.0401 |

The conductivity of a solution of magnesium chloride can be expressed in terms of the concentrations of the ions and their velocities, but the equation so obtained still contains two unknown quantities—the concentration and velocity of the MgCl' ions. By assuming that the most concentrated solution contains only MgCl' and Cl' ions, it is found that the maximum value of the velocity of the MgCl' ion is 23; the true value must therefore lie between 0 and 23. A consideration of the migration constants leads to the conclusion that the velocity is probably smaller than 10, and that the concentrations of the MgCl' ions are roughly represented by the following numbers:

| | | | | | |
|------------------------------------|-----|------|-----|------|------|
| Gram eq. MgCl_2 per litre | 2 | 1.5 | 1 | 0.5 | 0.1 |
| Gram eq. MgCl' per litre | 0.8 | 0.45 | 0.2 | 0.05 | 0.00 |

T. E.

Contribution to the Study of Dissolved Substances, III. AD. VANDENBERGHE (*Bull. Acad. roy. Belg.*, 1903, 908—947. Compare Abstr., 1900, ii, 335).—The influence exerted by different substances on the molecular association of compounds in various solvents is studied. By means of the boiling point method, it is shown that the introduction of a fresh substance, either associated or non-associated, to the solution of an associated compound usually causes the association of the latter to increase. The extent to which the association is influenced depends on the solvent used, the temperature, and the

concentration of the dissolved substances. The fact that such an influence can be exerted by the presence of foreign material causes the author to abandon his former view that an analogy holds between gaseous dissociation and the dissociation of substances in solution.

S. S.

Polymerisation of Liquid and Solid Inorganic Compounds.

GEORGE G. LONGINESCU (*Ann. sci. Univ. Jassy*, 1903, 11, 288—294. Compare Abstr., 1903, ii, 531).—By means of the relation $(T/C.D)^2 = n$, the author calculates the state of aggregation of about fifty inorganic substances, both liquid and solid; the observations are confined to compounds containing elements having atomic weights below 40. In general, the results agree with those obtained by other observers with different methods. The method cannot be applied to compounds which contain elements of very high atomic weight.

S. S.

The Phenomena of Solidification and Transformation in the Systems NH_4NO_3 , AgNO_3 , and KNO_3 , AgNO_3 .

H. W. BAKHUIS ROOZEBOM (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 259—262).—With mixtures of ammonium nitrate and potassium nitrate, the transition point of silver nitrate and the first transition point of ammonium nitrate falls in the region where these mixtures are still partially liquid; the two lower transition points of ammonium nitrate are situated in the region where everything has already become solidified. The deposition of silver nitrate from melted mixtures rich in silver takes place according to two lines, which meet each other at 160° ; the solidification of ammonium nitrate from mixtures rich in it also takes place along two lines, which meet each other at 125° . The salts are deposited pure and do not yield mixed crystals. From intermediate concentrations, a compound, NH_4NO_3 , AgNO_3 , is deposited, melting at 109.6° . The various phases involved are indicated in a diagram.

The system AgNO_3 , KNO_3 is simpler in so far that potassium nitrate has only one transition temperature at 126° . The transition point of silver nitrate falls within the partially liquid region. The various regions are also diagrammatically represented.

A. McK.

[Phase Rule.] RUDOLF WEGSCHEIDER (*Zeit. physikal. Chem.*, 1903, 45, 697—699).—Remarks relative to Byk's paper (this vol., ii, 16).

J. C. P.

Observations on the System Zinc Chloride, Ammonium Chloride, and Water. P. A. MEERBURG (*Zeit. anorg. Chem.*, 1903, 37, 199—221).—The purpose of this research was to determine which combinations of the components, zinc chloride, ammonium chloride, and water, are capable of existence at the ordinary temperature.

The binary systems, NH_4Cl , H_2O ; ZnCl_2 , H_2O ; ZnCl_2 , NH_4Cl , are first considered. The author has investigated the system NH_4Cl , H_2O , under 0° ; the cryohydric point is -16° , where the solution in contact with ice and solid ammonium chloride contains 19.5 per cent. of ammonium chloride. The results of Dietz on the solubility of zinc chloride in water are recapitulated.

The author has investigated by Schreinemaker's method the isothermals of the ternary system, $\text{ZnCl}_2, \text{NH}_4\text{Cl}, \text{H}_2\text{O}$, at 0° , 20° , and 30° , and expressed his results graphically. Of the eight double compounds of zinc chloride, ammonium chloride, and water quoted in the literature, only two are capable of existence at the ordinary temperature, namely, $\text{ZnCl}_2, 2\text{NH}_4\text{Cl}$ and $\text{ZnCl}_2, 3\text{NH}_4\text{Cl}$. The hydrates are capable of existence only at low temperatures, if at all. A. McK.

Negative Catalysis in a Homogeneous System. ALEXANDER TITOFF (*Zeit. physikal. Chem.*, 1903, 45, 641—683. Compare Bigelow, *Abstr.*, 1898, ii, 506).—The oxidation of sodium sulphite by dissolved oxygen takes place very slowly unless a catalytic agent is present. The reaction is of the first order, and the velocity of oxidation is within wide limits independent of the oxygen concentration. Many salts of heavy metals, notably copper sulphate, accelerate the oxidation, and the acceleration is approximately proportional to the amount of the catalyst. Mannitol acts as a negative catalyst, that is, it retards the oxidation of the sulphite, but about 1800 molecules of mannitol are required to counteract the effect of 1 molecule of copper sulphate. An inorganic negative catalyst has been found in stannic chloride (also stannous chloride), which exhibits the greatest retarding effect. The simultaneous effect of a positive catalyst (copper sulphate) and a negative catalyst (mannitol or stannic chloride) has been studied, and the experiments support the view that negative catalysis consists in a counteracting of the effect of positive catalysis. J. C. P.

Remarks on the Fifth Communication of the Committee on Atomic Weights. CLEMENS WINKLER (*Ber.*, 1903, 36, 4299—4302. Compare this vol., ii, 20).—Polemical. A. McK.

Comparative Studies in the Periodic System. The Various Gradation Stages between Elements. GEORGE RUDORF (*Zeit. anorg. Chem.*, 1903, 37, 177—198).—A theoretical paper which does not admit of abstraction. A. McK.

Determination of the Composition of Chemical Compounds without the Help of Analysis. GUSTAV TAMMANN (*Zeit. anorg. Chem.*, 1903, 37, 303—313).—The knowledge of the equilibrium of heterogeneous systems provides a means of deciding whether two substances form a compound with one another, and of determining the quantitative composition of the compound if it is produced. The method is based on the knowledge of the melting point diagram of two substances, and on the relationship between the properties of the molten mixture of the two substances and their composition; it is applicable in those cases where the mechanical separation of crystals from the molten mass in which they have separated, is practically impossible. Only those instances are considered where no mixed crystals are formed. A. McK.

Variation of Angles Observed in Crystals; especially of Potassium Alum, and Ammonium Alum. HENRY A. MIERS (*Phil. Trans.*, 1903, A, 202, 459—523).—Details of work already described (*Abstr.*, 1903, ii, 472). J. C. P.

Inorganic Chemistry.

Electrolytic Formation of Hydrogen Peroxide. FRANZ RICHARZ (*Zeit. anorg. Chem.*, 1903, 37, 75—79).—Historical and polemical. The formation of hydrogen peroxide at the anode during the electrolysis of sulphuric acid was first demonstrated by the author. Various statements made by Borneman (*Abstr.*, 1903, ii, 281) are corrected. A. MCK.

Density of Chlorine. HENRI MOISSAN and ARMAND BINET DU JASSONEIX (*Compt. rend.*, 1903, 137, 1198—1202).—Previous determinations of the density of chlorine have given numbers varying from 2.4482 to 2.491. Using the Dumas method, the authors have determined the density of pure chlorine obtained from sodium chloride purified by repeated crystallisations; the gas was dried in the usual way (*Abstr.*, 1903, ii, 642), then liquefied (*Abstr.*, 1902, ii, 66) and dried by prolonged contact with calcium chloride, and finally solidified in order to expel traces of dissolved gaseous impurities. The density at 0° of the chlorine gas thus purified was found to be 2.490. M. A. W.

Boiling of Sulphur, Selenium, and Tellurium in the Vacuum of the Cathode Light. FRIEDRICH KRAFFT and L. MERZ (*Ber.*, 1903, 36, 4344—4350).—In a former paper on the boiling points of the metals in the vacuum of the cathode-light (*Abstr.*, 1903, ii, 479), it was shown that selenium and tellurium boil at remarkably low temperatures. More detailed observations have now been made, electrically heated glass vessels being employed, and the temperatures being determined by a thermo-couple. Pure tellurium boils very constantly at 478° under a 58 mm. column of vapour, pure selenium boils at 310° under a 60 mm. column, the temperature rising slightly when rapidly superheated. Sulphur boils under similar conditions at about 140°, and the series of boiling points thus shows a constant difference; Te—Se = 168°, Se—S = 170°. The temperatures may readily be determined in glass flasks without an electric furnace, thermometers of borosilicate glass being used. The behaviour of sulphur was studied in greater detail, the sulphur being in some cases heated until it assumed the viscous state. The temperature of both liquid and vapour was measured.

| Height of column of vapour. | Temp. of vapour of normally boiling sulphur. | Temp. of vapour of colloidal sulphur. | Temp. of colloidal sulphur. |
|-----------------------------|--|---------------------------------------|-----------------------------|
| 40 mm. | 136—138° } Diff. | 183—187° } Diff. | 204—208° } Diff. |
| 115 „ | 151—152 } 15—14° | 199—202 } 16—15° | 223—225 } 19—17° |

The existence of the colloidal variety of sulphur is thus dependent on the pressure. The superheated vapour above the colloidal sulphur is influenced by the pressure of the column of vapour to the same extent as that from normal sulphur.

C. H. D.

Formula of Caro's Acid. MARTIN MUGDAN (*Zeit. Elektrochem.*, 1903, 9, 980).—Referring to Price's results (*Trans.*, 1903, 83, 543), the author points out that his own experiments (*Abstr.*, 1903, ii, 640) do not decide between the formulæ H_2SO_5 (monobasic) and $\text{H}_2\text{S}_2\text{O}_9$ (dibasic).

T. E.

Behaviour of Tellurium Compounds on being heated with Ammonium Chloride. ALEXANDER GUTBIER and FERDINAND FLURY (*Zeit. anorg. Chem.*, 1903, 37, 152—157).—When tellurium dioxide, telluric acid, or its alkali salts are heated with ammonium chloride, the mixture becomes yellow and then orange, whilst a white sublimate is formed. The mixture on being further heated, assumes a dark colour with the formation of a yellow sublimate, which blackens on careful heating. Tellurium finally remains as a brittle mass. These phenomena do not occur when ammonium chloride is replaced by ammonium nitrate, carbonate, sulphate, phosphate, acetate, or molybdate. The white sublimate obtained consisted partly of ammonium chloride and partly of the additive product, $\text{TeO}_2 \cdot 2\text{HCl}$. The black sublimate is probably a compound of tellurous chloride and ammonia, possibly $\text{TeCl}_2 \cdot 2\text{NH}_3$.

A. McK.

Synthesis of Ammonia. HERMANN CHARLES WOLTERECK (D.R.-P. 146712).—A mixture of hydrogen, nitrogen, and oxygen, or of atmospheric air with a gas containing hydrogen, such as water-gas, is passed over ferric oxide heated to low redness. The most suitable contact material is iron wire gauze which has been thoroughly oxidised. A mixture of equal parts of air and water-gas, containing a little steam, yields ammonia corresponding with 6.3 per cent. of the hydrogen employed. When coal-gas is used, the product which contains amines, must be purified by passing through a concentrated solution of alkali hydroxide.

The influence of ferric oxide in bringing about the combination of hydrogen and nitrogen is not merely catalytic, as the presence of oxygen is found to be essential to the reaction.

C. H. D.

Nitrohydroxylaminic Acid. ANGELO ANGELI and FRANCESCO ANGELICO (*Gazzetta*, 1903, 33, ii, 245—252).—Although the alkali salts of nitrohydroxylaminic acid, the salts of the alkaline earths, and of some of the heavy metals have been prepared, all attempts to prepare esters have failed. The silver salt, which is very unstable in neutral solution, can be obtained as a yellow powder by precipitating the sodium salt with silver nitrate in presence of a small quantity of acetic acid at 0° . On raising the temperature, it decomposes according to the equation $\text{OAg} \cdot \text{N} : \text{NO} \cdot \text{OAg} = \text{NO}_2\text{Ag} + \text{NO} + \text{Ag}$; practically

no hyponitrite is formed, although in the case of the sodium salt this is the principal product of decomposition. The free acid, on the other hand, decomposes according to the equation $\text{H}_2\text{N}_2\text{O}_3 = \text{H}_2\text{O} + 2\text{NO}$. There are thus six modes of decomposition of the acid and its salts: (1) $\text{H}_2\text{N}_2\text{O}_3 = 2\text{NO} + \text{H}_2\text{O}$; (2) $\text{H}_2\text{N}_2\text{O}_3 = \text{HNO}_2 + \text{N}\cdot\text{OH}$; (3) $\text{H}_2\text{N}_2\text{O}_3 = \text{HNO}_2 + \text{NO} + \text{H}$; (4) $\text{H}_2\text{N}_2\text{O}_3 + \text{H}_2\text{O} = \text{NH}_2\text{OH} + \text{HNO}_2 + \text{O}$; (5) $2\text{H}_2\text{N}_2\text{O}_3 = 2\text{HNO}_2 + (\text{NOH})_2$; (6) $2\text{H}_2\text{N}_2\text{O}_3 = 2\text{HNO}_2 + \text{N}_2\text{O} + \text{H}_2\text{O}$; (1) refers to the free acid; (2) to the sodium salt in presence of aldehydes, &c.; (3) to the silver salt alone; (4) to the hydrolysis of the hydroxamic acids formed by addition of the NOH to aldehydes in (2); (5 and 6) to the sodium salt.

Attempts to prepare nitrohydroxylaminic acid from hydroxamic acids by the reaction $\text{OH}\cdot\text{CR}\cdot\text{N}\cdot\text{OH} + \text{NO}\cdot\text{OH} = \text{OH}\cdot\text{NO}\cdot\text{N}\cdot\text{OH} + \text{R}\cdot\text{CHO}$ gave no issue.

Not only does nitrohydroxylaminic acid readily give up nitroxyl to aldehydes (this vol., i, 172), but the same is true of hydroxylamine-sulphonic acids of the type $\text{R}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{OH}$ (compare Abstr., 1902, i, 765). On the other hand, hyponitrous acid in the form of its sodium salt, which should react as 2NOH , fails to form hydroxamic acids with aldehydes or tetrazones with secondary bases. The authors compare the inactivity of $\text{HO}\cdot\text{N}\cdot\text{N}\cdot\text{OH}$ with that of molecular oxygen, $\text{O}\cdot\text{O}$.

W. A. D.

Preparation of Nitrites by the Electrolytic Reduction of Aqueous Solutions of Nitrates. ERICH MÜLLER and JULIUS WEBER (*Zeit. Elektrochem.*, 1903, 9, 955—967).—The platinum anode is enclosed in a porous pot in order to avoid oxidation of the nitrite formed. Smooth cathodes of platinum and copper are depolarised by solutions of sodium nitrate and of sodium nitrite, the latter being somewhat the better depolariser, although the results obtained are rather variable. With these cathodes, the electrolytic reduction yields a mixture of nitrite and ammonia.

A platinised platinum cathode is depolarised much more completely by a solution of sodium nitrite than by a solution of sodium nitrate, and the electrolytic reduction of a nitrate, therefore, yields much ammonia and very little nitrite. A cathode of spongy copper gives quite a different result, the depolarisation by nitrate being much more complete than that by nitrite. The depolarising effects of both solutions diminish, however, as the electrolysis is prolonged, their relative values finally being reversed. A momentary reversal of the current, however, brings them back to their initial values, and in this way a solution of sodium nitrate may be reduced to nitrite, and the formation of ammonia almost entirely avoided. The best current efficiency is obtained with a current density at the cathode of 0.0025 ampere per sq. cm., and a slightly alkaline solution of sodium nitrate containing 2.27 gram-mols. per litre; 66 per cent. of the nitrate in this solution was reduced to nitrite with a current efficiency of 90.8 per cent. The loss occurs mainly at the anode. Spongy copper slowly reduces nitrate to nitrite by a purely chemical process; the bearing of this fact on the difference between the behaviour of platinum and copper cathodes is discussed.

T. E.

Electrolytic Preparation of Nitrites from Nitrates. WOLF JOHANNES MÜLLER (*Zeit. Elektrochem.*, 1903, 9, 978).—The experiments are made with an amalgamated copper cathode, a platinum anode surrounded by a porous pot, a solution of sodium nitrate saturated at 80—90°, and a current density at the cathode of 0.005 to 0.01 ampere per sq. cm. The current efficiency was 85 to 92 per cent. until about 30 per cent. of the nitrate had been reduced to nitrite, but when 50 per cent. had been reduced, the current efficiency fell off to about 40 per cent. Attempts to separate the nitrate and nitrite by fractional crystallisation failed, the two salts crystallising together.

T. E.

Ionisation of Phosphorus. EUGÈNE BLOCH (*Compt. rend.*, 1903, 137, 1040—1042. Compare Abstr., 1903, ii, 206).—The value of α , the coefficient of recombination of phosphorus ions in a current of air which has passed over phosphorus, is 1000 times more feeble than the corresponding coefficient for the case of ionisation by the Röntgen rays. The value of ϵ , the ratio of the number of recombinations to the total number of collisions between the ions of opposite signs (compare Langevin, Abstr., 1902, ii, 301), lies between 0.7 and 1. The independent measurements of the mobility (Abstr., 1903, ii, 206), of the coefficient of recombination, and of the ratio ϵ for the ions of phosphorus give perfectly concordant results, which affords strong evidence in favour of a true ionisation.

M. A. W.

Phosphorus. II. RUDOLF SCHENK (*Ber.*, 1903, 36, 4202—4209. Compare Abstr., 1903, ii, 363).—The black substance formed by the action of piperidine on solid hydrogen phosphide, on analysis gives figures between those required by the formula $P_4H_2(C_5H_{11}N)$ and $P_5H_2(C_5H_{11}N)$; that is, it is a salt of the hydride, P_4H_2 , containing a small quantity of phosphorus; the results previously obtained were due to the piperidine used not being sufficiently dried. The black ammonium salt previously described has the composition $P_4H_2NH_3$. The fact that ammonia produces no black coloration with solid hydrogen phosphide is due to the small velocity with which the change takes place; on warming slightly, the black colour appears. The measurements previously made in studying the conversion of white phosphorus into red have been repeated and the change is now shown to be unimolecular; the previous false assumption of a bimolecular change was caused by the mechanical removal of the catalytic agent, phosphorus iodide, from the solution by the red phosphorus.

E. F. A.

Solubility of Arsenic and the Molecular Condition of the Solution. LUDWIK BRUNER and STANISLAW TOLLOCZKO (*Zeit. anorg. Chem.*, 1903, 37, 455—458).—By means of the apparatus previously described (Abstr., 1903, ii, 470), the authors have determined the solubility of arsenious oxide in water. The equilibrium between the oxide and the solution established itself slowly in every case. The molecular weight of arsenious acid in aqueous solution is expressed not by $As_2O_3 + xH_2O$, but by $\frac{1}{2}As_2O_3 + yH_2O$.

A. McK.

Action of Magnesium Oxide on a Mixture of Arsenic Trisulphide and Sulphur. WILLIAM FOSTER, jun. (*Zeit. anorg. Chem.*, 1903, 37, 59—68).—When magnesium oxide acts on a mixture of arsenic trisulphide (1 mol.) and sulphur (2 atoms) in presence of water, traces of magnesium monothio-oxyarsenate are formed together with magnesium thioarsenate and magnesium dithio-oxyarsenate (McCay, *Abstr.*, 1902, ii, 135). The author has made a further study of McCay's work in this direction.

By the action of magnesium oxide on a mixture of arsenic trisulphide and sulphur in aqueous suspension, a mixture of compounds is formed, the relative proportions of which depend on the experimental conditions. At the ordinary temperature a small amount of monothio-oxyarsenic acid is formed, and a large amount of *trithio-oxyarsenic acid*, of which the *sodium* salt, $\text{Na}_3\text{AsOS}_3 \cdot 9\text{H}_2\text{O}$, was isolated. Dithio-oxyarsenic and thioarsenic acids were also present. The amount of monothio-oxyarsenic acid formed increases with rise of temperature during the interaction, whilst at 70° more dithio-oxyarsenic acid is present than at 100°.

A. McK.

Boric Acid and Arsenious Acid. A Study on the Formation of Complexes. FRIEDRICH AUERBACH (*Zeit. anorg. Chem.*, 1903, 37, 353—377).—Dilute borax solutions, in addition to sodium ions, contain monoborate ions and free boric acid, whilst in more concentrated solutions the latter form complex polyborate ions, which are broken up by addition of water or sodium hydroxide. In order to determine the amount of free boric acid in such solutions, the author allows boric acid to compete with another weak acid, arsenious acid, in the presence of an insufficiency of base.

Arsenious acid is soluble in amyl alcohol; it distributes itself between amyl alcohol and water in the constant proportion 1:5.47. With excess of arsenious acid, arsenite ions unite to form diarsenite ions and, possibly, also more complex ions. The tendency to the formation of complexes is only moderately great, so that at 25°, with an excess of 0.2*N* arsenious acid, at least half of the salt is in the form of monoarsenite.

Diarsenious acid is a stronger acid than arsenious acid, but is capable of existence in the free state only in very small concentrations. The electrolytic dissociation constant of the complex acid is in the same proportion to that of the simple acid as the constant for the decomposition of the complex of the undissociated acid is to that of its ion. Borate ions unite with excess of boric acid to form polyborate ions; the tendency of the formation of such polyborate ions is great. The type of polyborate ion depends on the concentration of the boric acid in the solution; in the presence of saturated boric acid solutions at 25°, the complexes on an average contain 5 atoms of boron to 1 electron. The polyboric acids are stronger than monoboric acid and than arsenious acid, and they are capable of existence in the free state at low temperatures and in high concentrations.

In a mixture of boric and arsenious acids containing an insufficiency of sodium hydroxide for complete neutralisation, a complicated condition of equilibrium is established between the two simple acids,

several complex acids, and their salts. The relationship in amount of the total borate to the total arsenite in such a solution is accordingly dependent on the extent to which both acids form complex compounds. A. McK.

Thomsen's Supposed Synthesis of Carbon Monosulphide, CS. ALFRED STOCK and HANS KÜCHLER (*Ber.*, 1903, 36, 4336—4339).—The increase in the volume of the nitrogen observed by Thomsen in his experiments (*Abstr.*, 1903, ii, 288) is shown to be due not to the formation of carbon monosulphide but simply to carbon disulphide vapour, the tension of which is high because of the temperature due to the proximity of the heated tube; that this is so can be shown by cooling the gas in liquid air, when solid carbon disulphide is obtained. There is also present a considerable quantity of carbon dioxide, which on cooling solidifies; its presence is due to the fact that metallic copper is never free from oxide, which oxidises some of the carbon disulphide employed. W. A. D.

Distillation of Hydrofluosilicic Acid. EMIL BAUR (*Ber.*, 1903, 36, 4209—4214).—Hydrofluosilicic acid solutions of different concentrations were distilled and the amount of hydrofluoric, hydrofluosilicic, and silicic acids in the distillate estimated in each case. An acid containing 13·3 per cent. of hydrofluosilicic acid gives a vapour, the composition of which is exactly expressed by the formula H_2SiF_6 . The distillate from more concentrated acids contains silicic acid, whilst dilute acids yield a distillate containing hydrogen fluoride; further, concentrated acids dissolve silicic acid when evaporated with it, whereas dilute solutions deposit this acid on evaporation. An acid containing 30·2 per cent. of hydrofluosilicic acid boils at 108·5° under 720 mm. pressure. E. F. A.

Vapour Density of Hydrofluosilicic Acid. EMIL BAUR and ARTHUR GLAESSNER (*Ber.*, 1903, 36, 4215—4218).—The volume of a weighed amount of hydrofluosilicic acid was measured at various pressures at temperatures of 23°, 31·5°, and 42°. Under the conditions of the experiment, the observed molecular weight was roughly 80, showing that more than half of the hydrofluosilicic acid was dissociated, and it is probable that at 100° more than two-thirds are dissociated. E. F. A.

Action of Hydrogen Sulphide on Silicon Tetrabromide in presence of Aluminium Bromide; Formation of Silicon Thiourea from Silicon Thiobromide. MARTIN BLIX (*Ber.*, 1903, 36, 4218—4220).—*Silicon thiobromide*, $SiSBr_2$, formed by the interaction of silicon tetrabromide and hydrogen sulphide at 150° in presence of aluminium bromide, boils without decomposition at 150° under 18·3 mm. pressure and solidifies to large, colourless plates melting at 93°. When dry ammonia is passed through its benzene solution, a mixture of *silicon thiourea* [*silicon thiodiamide*] and ammonium bromide is precipitated, from which the soluble ammonium bromide is extracted with liquid ammonia. Silicon thiourea is a colourless, amorphous

powder relatively stable in the air; it has basic properties and forms salts with the halogen acids.

Pure silicon tetrabromide melts at $+5^{\circ}$ and boils at 150.8° under 751.4 mm. pressure. E. F. A.

Silicon Thiochloride, Silicondi-imide, Silicam, and Silicon Nitride. MARTIN BLIX and W. WIRBELAUER (*Ber.*, 1903, 36, 4220—4228).—Silicon tetrachloride and hydrogen sulphide form a compound $\text{SiCl}_3\cdot\text{SH}$ (Pierre, *Ann. Chim. Phys.*, 1848, [iii], 24, 286; Friedel and Ladenburg, *Annalen*, 1868, 145, 179), boiling at 96° ; this, when heated to a higher temperature by passing through a glass tube at a dull red heat, the apparatus being so arranged that the gases continually circulate in a closed circuit, is converted into *silicon thiochloride*, SiSCl_2 , which crystallised from chloroform, melts at 75° , and distils at 92° under 22.5 mm. pressure; it is very easily decomposed by moisture or by distillation at the ordinary temperature into silicon disulphide and silicon tetrachloride. Liquid anhydrous ammonia reacts with either silicon disulphide or still more readily with the thiochloride forming *silicondi-imide*, $\text{Si}(\text{NH})_2$, but the product always contains 2—3 per cent. of sulphur. The imide is obtained pure by the action of ammonia on the ammoniosilicon chloride, $\text{SiCl}_4\cdot 6\text{NH}_3$, prepared by Persoz (*Annalen*, 1842, 44, 319); so prepared, it forms a colourless, non-fusible powder which slowly decomposes into silica and ammonia on exposure to air; it has basic properties and forms a relatively stable hydrochloride, $\text{Si}(\text{NH})_2\cdot 2\text{HCl}$. When heated at 900° in an atmosphere of nitrogen, it loses ammonia, forming silicon nitrimide (silicam), $\text{Si}_2\text{N}_3\text{H}$ (compare Schützenberger and Colson, *Abstr.*, 1882, 571), an amorphous powder, which is not acted on by water and when heated at 1200 — 1300° loses ammonia forming silicon nitride, Si_3N_4 . E. F. A.

Coagulation of Colloidal Silicic Acid. NICOLA PAPPADÀ (*Gazzetta*, 1903, 33, 272—276).—Tables are given showing the time of coagulation of 0.6 and 3.9 per cent. solutions of silicic acid. From these it is concluded that the time of coagulation is diminished by increasing the concentration of the coagulating salts, and is dependent on the nature of these. Acids, acid salts, and salts with an acid reaction in solution either fail altogether to coagulate the solutions or, with some concentrated solutions, the coagulation is very slow. Neutral salts cause rapid coagulation, and their effect is greater the greater their molecular weight. Salts with an alkaline reaction are most rapid in their action. W. A. D.

Decomposition of Crystallised Sodium Thiosulphate by Heat. ARTHUR JAQUES (*Chem. News*, 1903, 88, 295).—When crystallised sodium thiosulphate is heated quickly in a test-tube, hydrogen sulphide is evolved, and sulphur, sodium sulphite, and sodium sulphate are present in the residue. D. A. L.

Electrolytic Preparation of Alkali Selenates. ERICH MÜLLER (*Ber.*, 1903, 36, 4262—4266).—Foerster and Friessner have shown (*Abstr.*, 1902, ii, 488) that during the electrolysis of sulphites, oxidation occurs with the formation not only of SO_4 ions but also of S_2O_6 ions. The author has studied the electrolysis of selenites and has observed that, whilst selenates are readily formed by the electrolytic oxidation, there is no formation of selenium salts corresponding with dithionates.

A neutral solution of sodium selenite is electrolysed until all the selenite has disappeared, that is, until a portion of the electrolyte causes no separation of iodine and selenium with a solution of potassium iodide. The anode consists of platinum foil, the cathode of platinum wire. Sodium selenate is then obtained by simply evaporating the solution, after filtering it from a small amount of selenium. In the presence of potassium chromate, the deposition of selenium at the cathode is entirely prevented. In order to obtain sodium selenate from the latter solution, the chromium must first of all be removed by precipitation, so that, on the whole, the method of preparing the selenate by electrolysing the selenite in the absence of potassium chromate is to be preferred.

When a neutral solution of sodium selenite or of sodium selenate is electrolysed, a slight deposition of selenium on the cathode occurs in both cases, but the deposition ceases after some time.

On electrolysis, faintly alkaline solutions of sodium tellurite and tellurate respectively undergo considerable reduction to tellurium.

A. McK.

Dissociation of Alkali Carbonates. PAUL LEBEAU (*Compt. rend.*, 1903, 137, 1255—1257).—Contrary to his original conclusion (compare *Abstr.*, 1903, ii, 477), the author now finds that the carbonates of all the alkali metals are dissociated into carbon dioxide and a volatile alkali oxide by heating them in a vacuum below 800° .

Sodium carbonate begins to dissociate at 700° and can be completely volatilised at 1000° .

Potassium carbonate begins to dissociate at 790° and volatilisation is complete at 1000° .

Rubidium carbonate, prepared from the pure platinichloride through the chloride, sulphate, hydroxide, and hydrogen carbonate, begins to dissociate at 740° and, like the corresponding compound of sodium and potassium, can be completely volatilised at 1000° .

Cæsium carbonate (which forms the crystalline hydrate $3\text{Cs}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) begins to dissociate at 600° , and below 1000° its volatility is comparable with that of lithium carbonate.

If the alkali metals are arranged in the two sub-groups (1) lithium and sodium, (2) potassium, rubidium, and cæsium, it is seen that the readiness with which their carbonates dissociate decreases with the atomic weight in the first group and increases in the second.

M. A. W.

Composition of Bredig's Silver Hydrosols. J. C. BLAKE (*Amer. J. Sci.*, 1903, [iv], 16, 431—432).—In preparing silver hydrosols

according to Bredig's method, the author observed that the anode was eroded fully as much as the cathode, and the freshly prepared liquid was distinctly alkaline. The erosion of the anode under conditions described in the paper was measured.

Silver compounds are possibly formed during the preparation of silver hydrosols according to Bredig's method. A. McK.

Colloidal Silver. ALLYRE CHASSEVANT (*Bull. Soc. chim.*, 1904, [iii], 31, 6—11).—The author disputes the idea advanced by Hanriot (*Abstr.*, 1903, ii, 368) that collargol is an acid (collargollic acid).

S. S.

Preparation and Properties of Pure Colloidal Silver. ALLYRE CHASSEVANT (*Bull. Soc. chim.*, 1904, [iii], 31, 11—13).—Using Schneider's method (*Abstr.*, 1892, 775), an alcoholic solution of colloidal silver was prepared, and was found to have the properties already ascribed to it by various authors. S. S.

Behaviour of Manganous Salts towards Silver Peroxide. OTTO KUHLLING (*Zeit. angew. Chem.*, 1903, 16, 1145—1150).—The action of silver peroxide nitrate, $2\text{Ag}_3\text{O}_4 \cdot \text{AgNO}_3$, prepared by the electrolysis of silver nitrate, on ammonium manganese sulphate, $\text{MnSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, has been examined. The oxidation of manganous solutions by silver peroxide and nitric acid is slow in the cold. The solutions are at first coloured owing to the formation of permanganate; they gradually become colourless and manganese dioxide separates. On the continued addition of silver peroxide, the pink colour of the solution does not disappear until the solution is heated, and finally the colour is persistent, a clear solution of permanganic acid being formed.

The separation of the manganese as dioxide is in certain cases quantitative.

The permanganic acid, formed under conditions where no separation of manganese dioxide took place, was estimated by aid of hydrogen peroxide. A. McK.

Complex Metallic Compounds. GUIDO BODLÄNDER (*Ber.*, 1903, 36, 3933—3945. Compare *Abstr.*, 1902, ii, 63; Bodländer and Fittig, *ibid.*, 248; Bodländer and Storbeck, *ibid.*, 502 and 607; Sherrill, *Abstr.*, 1903, ii, 534 and 649; Bonsdorff, *ibid.*, 598; Euler, *ibid.*, 717).—A discussion of experimental results which are to be published in detail elsewhere. Tables I and II give the constants governing the stability of complex metallic salts in solution as determined by methods which have already been described (*loc. cit.*).

TABLE I.

| Formula of the complex ion. | Concentration limits of the free anions. | Stability constant. | Heat of formation of 1 gram-equiv. from the simple ions in Cal. |
|--|--|-----------------------|---|
| $\text{Ag}(\text{S}_2\text{O}_3)_2'''$ | below 0.1 <i>N</i> | $0.98 \cdot 10^{13}$ | $17200 + 1340 \log[\text{Ag}][\text{S}_2\text{O}_3]^2/\text{D}$ |
| $\text{Ag}(\text{S}_2\text{O}_3)_3^v$ | above 0.5 <i>N</i> | $3.45 \cdot 10^{13}$ | $18000 + 1340 \log[\text{Ag}][\text{S}_2\text{O}_3]^3/\text{D}$ |
| $\text{Ag}(\text{CN})_2$ | under 0.05 <i>N</i> | $0.11 \cdot 10^{22}$ | $27900 + 1340 \log[\text{Ag}][\text{CN}]^2/\text{D}$ |
| $\text{Ag}_2\text{I}_4''$ to AgI_4''' | indefinite limits | $7.7 \cdot 10^{13}$ | $18460 + 1340 \log[\text{Ag}][\text{I}]^4/\text{D}$ |
| $\text{Ag}(\text{CNS})_2$ | below 0.2 <i>N</i> | $6 \cdot 10^9$ | $13000 + 1340 \log[\text{Ag}][\text{CNS}]^2/\text{D}$ |
| $\text{Ag}(\text{CNS})_4'''$ | above 0.3 <i>N</i> | $1.5 \cdot 10^{11}$ | $14850 + 1340 \log[\text{Ag}][\text{CNS}]^4/\text{D}$ |
| $\text{Hg}(\text{CN})_4'''$ | in all concentrations | $5.05 \cdot 10^{20}$ | $27500 + 670 \log[\text{Hg}][\text{CN}]^4/\text{D}$ |
| $\text{Au}(\text{CN})_2'$ | " " | $> 2.5 \cdot 10^{29}$ | $> 39000 + 1340 \log[\text{Au}][\text{CN}]^2/\text{D}$ |
| $\text{Cu}(\text{CN})_3''$ | indefinite limits | $5.6 \cdot 10^{26}$ | $35500 + 1340 \log[\text{Cu}][\text{CN}]^{3.5}/\text{D}$ |
| $\text{Cu}(\text{CN})_4'''$ | | | |
| $\text{Zn}(\text{CN})_3''$ | " " | $5.7 \cdot 10^8$ | $11600 + 670 \log[\text{Zn}][\text{CN}]^2/\text{D}$ |
| $\text{Zn}(\text{CN})_4'''$ | | | |
| HZnO_2' | in all concentrations | $1.9 \cdot 10^6$ | $8340 + 670 \log[\text{Zn}][\text{OH}]^2/\text{D}$ |
| $\text{Zn}(\text{C}_2\text{O}_4)_2''$ | below 0.1 <i>N</i> | $1.9 \cdot 10^3$ | $4360 + 670 \log[\text{Zn}][\text{C}_2\text{O}_4]^2/\text{D}$ |
| $\text{Zn}(\text{C}_2\text{O}_4)_3'''$ | above 0.1 <i>N</i> | $1.8 \cdot 10^4$ | $5650 + 670 \log[\text{Zn}][\text{C}_2\text{O}_4]^3/\text{D}$ |

The logarithms are to base 10, and D denotes the concentration of the complex ion in gram-mols., not equivalents.

TABLE II.

| Formula. | Tension of the solution for the metal with reference to the H-electrode. | Heat of formation in Cal. of 1 gram-ion of the complex from the metal and the anions. |
|--|--|---|
| $\text{Ag}(\text{S}_2\text{O}_3)_2'''$ | $-0.022-0.058 \log \text{D} : [\text{S}_2\text{O}_3]^2$ | $-512-1340 \log \text{D} : [\text{S}_2\text{O}_3]^2$ |
| $\text{Ag}(\text{S}_2\text{O}_3)_3^v$ | $+0.009-0.058 \log \text{D} : [\text{S}_2\text{O}_3]^3$ | $+209-1340 \log \text{D} : [\text{S}_2\text{O}_3]^3$ |
| $\text{Ag}(\text{CN})_2$ | $+0.444-0.058 \log \text{D} : [\text{CN}]^2$ | $+10330-1340 \log \text{D} : [\text{CN}]^2$ |
| $\text{Ag}(\text{CN})_3''$ | $+0.497-0.058 \log \text{D} : [\text{CN}]^3$ | $+11560-1340 \log \text{D} : [\text{CN}]^3$ |
| $\text{Ag}_2\text{I}_4''$ to AgI_4''' | $+0.054-0.058 \log \text{D} : [\text{I}]^4$ | $+1250-1340 \log \text{D} : [\text{I}]^4$ |
| $\text{Ag}(\text{CNS})_2$ | $-0.197-0.058 \log \text{D} : [\text{CNS}]^2$ | $-4600-1340 \log \text{D} : [\text{CNS}]^2$ |
| $\text{Ag}(\text{CNS})_4'''$ | $-0.116-0.058 \log \text{D} : [\text{CNS}]^4$ | $-2700-1340 \log \text{D} : [\text{CNS}]^4$ |
| $\text{Hg}(\text{CN})_4'''$ | $+0.384-0.029 \log \text{D} : [\text{CN}]^4$ | $+17860-1340 \log \text{D} : [\text{CN}]^4$ |
| $\text{Au}(\text{CN})_2$ | $+0.611-0.058 \log \text{D} : [\text{CN}]^2$ | $+14210-1340 \log \text{D} : [\text{CN}]^2$ |
| $\text{Cu}(\text{CN})_3''$ and $\text{Cu}(\text{CN})_4'''$ | $+1.098-0.058 \log \text{D} : [\text{CN}]^{3.5}$ | $+25550-1340 \log \text{D} : [\text{CN}]^{3.5}$ |
| $\text{Zn}(\text{CN})_3''$ and $\text{Zn}(\text{CN})_4'''$ | $+1.287-0.029 \log \text{D} : [\text{CN}]^3$ | $+59900-1340 \log \text{D} : [\text{CN}]^3$ |
| HZnO_2' | $+1.130-0.029 \log \text{D} : [\text{OH}]^2$ | $+52600-1340 \log \text{D} : [\text{OH}]^2$ |
| $\text{Zn}(\text{C}_2\text{O}_4)_2''$ | $+0.988-0.029 \log \text{D} : [\text{C}_2\text{O}_4]^2$ | $+46000-1340 \log \text{D} : [\text{C}_2\text{O}_4]^2$ |
| $\text{Zn}(\text{C}_2\text{O}_4)_3'''$ | $+1.017-0.029 \log \text{D} : [\text{C}_2\text{O}_4]^3$ | $+47300-1340 \log \text{D} : [\text{C}_2\text{O}_4]^3$ |

For a detailed discussion of these numbers, the original should be consulted.

W. A. D.

New Method of preparing some Anhydrous Crystalline Fluorides. EDOUARD DEFACQZ (*Compt. rend.*, 1903, 137, 1251—1253. Compare Poulenc, *Abstr.*, 1894, ii, 234).—When a mixture of ten parts of calcium chloride and one part of manganous fluoride (compare

Moissan and Venturi, *Abstr.*, 1900, ii, 405) is fused in an atmosphere of carbon dioxide at 1000—1200°, double decomposition occurs, and after treating the fused mass with water to remove the manganous chloride and unchanged calcium chloride, and with dilute hydrochloric acid to remove oxidation products, the calcium fluoride is obtained in the form of crystals, the shape of which vary with the temperature of the fusion, being octahedra when the fusion has been effected at 800—1000°, and perfect cubes when the temperature of the fusion has been 1200—1400°. The reaction between manganous fluoride and calcium chloride is partly reversible, calcium fluoride reacting with manganous chloride to yield calcium fluorochloride; for this reason, it is necessary to have a large excess of calcium chloride in preparing crystalline calcium fluoride by this method. M. A. W.

Preparation of Barium Nitrite. OTTO N. WITT and KURT LUDWIG (*Ber.*, 1903, 36, 4384—4389. Compare Matuschek, *Chem. Ind.*, 1902, 25, 207).—Equivalent quantities of dry sodium nitrite and barium chloride are intimately mixed and added to sodium nitrite (1 equivalent) dissolved in 3 times its weight of boiling water. By using an excess of sodium nitrite, the "salting out" of part of the barium chloride before the reaction is complete is prevented. The precipitated sodium chloride is immediately removed by a hot filter, and on cooling the filtrate, well-defined crystals of barium nitrite, $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$, are obtained. They are best removed by the aid of a good centrifuge. The mother liquor, which contains the excess of sodium nitrite, may be used again. When heated, it begins to evolve oxides of nitrogen at 115°. J. J. S.

The Non-precipitability of Magnesium by Ammonia in the presence of Ammonium Salts. FREDERICK P. TREADWELL (*Zeit. anorg. Chem.*, 1903, 37, 326—331).—A series of physico-chemical experiments which confirm Loven's statement (*Abstr.*, 1896, ii, 413) that the non-precipitation of magnesium (and similar elements) by ammonia in the presence of ammonium salts is not due to the formation of a complex salt, but solely to the retardation of the dissociation of the ammonium hydroxide by the ammonium chloride according to the law of mass action. L. DE K.

Formation of Red Lead by Light and Air. GEORG KASSNER (*Arch. Pharm.*, 1903, 241, 696—708).—A specimen of lead monoxide (massicot) was exposed to direct sunlight during eight years in a bottle which was shaken and opened frequently; it had then turned red, and was found to contain available oxygen. Of the red powder, 43.1 per cent. could be extracted with a concentrated solution of lead acetate; the amount of available oxygen in it corresponded with a percentage of 18.8 PbO_2 in the residue, which therefore must have had a composition lying between Pb_5O_6 and Pb_6O_7 . A product containing available oxygen was also obtained when well dried massicot was exposed to sunlight in a sealed glass tube; the residual air contained only 11.2 per cent. of oxygen. Evidently moisture is not concerned in the oxidation.

It is suggested that the oxidation consisted in the addition of atomic oxygen, resulting from ionisation of the gas under the influence of the light in immediate contact with the coloured substance. In support of this view, an experiment is described in which massicot was converted into a brown substance containing available oxygen by passing ozonised oxygen over it. It is thought that the suggested explanation may apply to other cases of autoxidation. C. F. B.

Decomposition of Mercurous Chloride by Solutions of Alkali Chlorides. JUL. GEWECKE (*Zeit. physikal. Chem.*, 1903, 45, 684—696. Compare Richards and Archibald, *Abstr.*, 1902, ii, 384; Sherrill, *Abstr.*, 1903, ii, 534).—When mercurous chloride is shaken with concentrated solutions of sodium, potassium, or ammonium chloride (at 25°, 35°, and 45°), mercuric chloride and mercury are formed, the extent of the action increasing with the temperature and the concentration of the alkali chloride. The mercuric chloride probably exists as a double salt (compare Le Blanc and Noyes, *Abstr.*, 1890, 388), and it is supposed that this double salt is practically undissociated in presence of the great excess of alkali chloride, and that the action (with sodium chloride) may be represented by the equation : $\text{Na}^+ + \text{Na}^+ + \text{Cl}^- + \text{Cl}^- + \text{Hg}_2\text{Cl}_2 = \text{Na}_2\text{HgCl}_4 + \text{Hg}$. The mass action law then requires $c_1/c^2 = K$, where c_1 is the concentration of the double salt, and c that of the chlorine ions. The values of K obtained in this way tend to diminish as the concentration of the alkali chloride increases.

It is shown that mercury dissolves slightly when shaken with an alkali chloride in presence of air, and this must be allowed for in considering the action of alkali chloride on mercurous chloride.

In spite of the above observations, the use of calomel electrodes in concentration cells is permissible, provided the alkali chloride solutions are dilute. It is further advisable to use air-free solutions, and to keep the temperature down. J. C. P.

Preparation of Cerium Dioxide and its Reduction in a Current of Hydrogen. RICHARD JOSEPH MEYER (*Zeit. anorg. Chem.*, 1903, 37, 378—393).—For the preparation of pure cerium dioxide, the author uses the commercial mixture of oxalates from monazite sand, from which the thorium has been extracted; in some cases, Swedish cerite is employed. The material is first converted into the crystallised ammonium double nitrate, the solution of which, after having first been treated with hydrogen sulphide, is warmed at 60—70° with pure hydrogen peroxide, whereby the thorium and cerium peroxide are quantitatively removed. The dissolved cerium is then precipitated by magnesium acetate and hydrogen peroxide, and the basic acetate so obtained converted into cerium ammonium nitrate, which is repeatedly crystallised from nitric acid. The oxalate is next prepared and converted into the oxide, from which the sulphate is obtained. In order to free the latter from the trace of lanthanum it contains, it is acted on by potassium permanganate and sodium carbonate, and acidified by nitric acid. The residue is treated with a mixture of hydrochloric and oxalic acids, whereby cerium oxalate is

obtained, which, on being heated to redness, yields an oxide completely free from lanthanum. The slight coloration exhibited by the oxide after this treatment is completely removed by treating the solution with sulphurous and hydrochloric acids.

Pure cerium dioxide is faintly yellow. The colour becomes more intense when the dioxide is heated; this is probably due to polymerisation, but not to reduction.

The reduction of cerium dioxide by hydrogen takes place only in the complete absence of air. With increasing temperature, the colour of the oxide changes to greenish and then to a bluish-black tint. The constitution of the blue oxide obtained has not yet been determined. The quantitative determinations quoted show that the sesquioxide, Ce_2O_3 , is not formed by the reduction of cerium dioxide by hydrogen.

A. McK.

Series of Artificial Quadratic Spinel of the Hausmannite Type. I and II. ALEXANDRE GORGEU (*Bull. Soc. chim.*, 1903, [iii], 29, 1111—1117; 1167—1174).—The author has previously assigned to manganate and hausmannite the formulæ, $\text{MnO}_2, \text{MnO}, \text{H}_2\text{O}$, and $\text{MnO}_2, 2\text{MnO}$ respectively, since these minerals were partially soluble in nitric acid, leaving a residue of manganese dioxide. He now finds that when hausmannite is treated with dilute acetic acid, 2/3 of the manganese is obtained as a residue of manganese sesquioxide, the remainder passing into solution as manganese acetate, whilst manganite is unchanged by this treatment, indicating that hausmannite should be represented by the formula $\text{Mn}_2\text{O}_3, \text{MnO}$ and manganite by $\text{Mn}_2\text{O}_3, \text{H}_2\text{O}$.

When manganous, sodium, and zinc sulphates are fused together and the resulting product is washed with water and dilute acetic acid, there is obtained a crystalline residue having the composition $\text{Mn}_2\text{O}_3, \text{ZnO}$, and crystallographic and optical properties similar to those of hausmannite. Similar compounds have been prepared in which the manganous oxide of hausmannite is partially replaced by magnesium or cadmium oxides, but no definite products containing nickelous or cobaltous oxide could be isolated owing to the insolubility of the by-products obtained in these two cases in dilute acetic acid.

Products of this character may also be prepared by ignition of the metallic manganites formed by the digestion of freshly precipitated hydrated manganese dioxide in aqueous solutions of neutral salts.

The manganates of magnesium, $\text{MgO}, 4\text{MnO}_2$, zinc, $\text{ZnO}, 3\text{MnO}_2$, cadmium, $\text{CdO}, 5\text{MnO}_2$, and nickel, $\text{NiO}, 5\text{MnO}_2$, thus prepared, furnished on ignition, products containing respectively 7.54, 7.01, 6.35, and 7.22 per cent. of "active" oxygen, that is, oxygen not present in the form of metallic protoxides, whereas if the products had consisted merely of admixtures of Mn_2O_3 with the oxides of the various metals, only 6.09, 5.42, 5.29, and 5.92 per cent. respectively of "active" oxygen would have been found. Whence the author concludes that a mixed oxide of the type $\text{Mn}_2\text{O}_3, \text{MO}$ was formed in each of these cases and also by the ignition of copper manganite, $\text{CuO}, 4\text{MnO}_2$, and cobalt manganite, $\text{CoO}, 6\text{MnO}_2$, similarly prepared. No mixed oxides were obtained by igniting manganites of potassium or barium.

When freshly precipitated hydrated manganese dioxide is digested in a hot aqueous solution of cobalt sulphate, part of the manganese is dissolved, and the insoluble product obtained consists of cobalt manganocobaltite, which on ignition at a red heat furnishes a product which is not a mixture of the oxides Mn_3O_4 and Co_3O_4 , since the latter is unstable at a red heat; the author regards it as a complex oxide of the formula $Mn_2O_3Co_3O_3, MnOCO$. The ignition of a ferric manganite, $Fe_2O_3, 12MnO_2$, gave a product containing Fe_2O_3, MnO .

These results indicate that oxides of the hausmannite type may be obtained in which manganese may be partially replaced by other metals both in the acidic (sesquioxide) and basic (protoxide) portions of the molecule; the metals capable of so replacing the manganese are those which occur in the natural spinels of the regular system.

T. A. H.

Electrolytic Preparation of Metallic Permanganates. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P 145368).—The metallic permanganates, which are not readily obtained from potassium permanganate by double decomposition, may be prepared electrolytically. A closed electrolytic cell, with suitable diaphragm and provided with tubes for the escape of gases, is employed. In the preparation of calcium permanganate, for instance, the cathode cell contains a dilute solution of potassium hydroxide. The anode cell contains potassium permanganate solution, kept saturated by suspended baskets of the salt. During the electrolysis, lime is added to this cell from time to time in the form of a cream. Hydrogen is evolved at the cathode and oxygen at the anode, the permanganic acid formed combining with the lime. After a time, the calcium and potassium permanganates remaining are separated by crystallisation. Calcium chloride may be used in place of lime, in which case the cathode cell is filled with a saturated solution of potassium chloride.

C. H. D.

New Method of Determining the Critical Points of Iron and Steel. OCTAVE BOUDOUARD (*Compt. rend.*, 1903, 137, 1054—1056).—A preliminary note describing the modification of Saladin's apparatus employed in the determination of the critical points of iron and its alloys. No results are given.

M. A. W.

Influence of Pressure on the Transition Temperatures of Iron. GUSTAV TAMMANN (*Zeit. anorg. Chem.*, 1903, 37, 448—454).—At 770° , α -iron passes into the β -form, which at 890° is transformed with contraction into the γ -form. These transformations are reversible, and the influence of pressure on the transition temperature may be calculated by aid of the Clausius-Clapeyron formula, $dT/dp = \Delta vT/Rp$. In the transformation of the α - into the β -form, the value $dT/dp = 0$, that is, the temperature of the transformation is independent of the pressure. At 770° under a pressure of 12,000 kilo. per sq. cm., the transition curves of the α - into the β -form and of the β - into γ -forms cut one another at a triple point, where α -, β -, and γ -iron are in equilibrium.

With 0.3 per cent. of carbon, the same transition of γ - into α -iron can be effected as under a pressure of 12,000 kilos. in the absence of carbon.

A. McK.

Constitution and Properties of Silicon Steels. LÉON GUILLET (*Compt. rend.*, 1903, 137, 1052—1054).—According to their micrographical properties, steels containing silicon may be divided into three groups: (1) steels containing 0—5 per cent. of silicon, in which all the carbon is in combination. (2) Steels containing 5—7 per cent. of silicon, in which the carbon is partly combined and partly in the form of graphite. (3) Steels containing more than 7 per cent. of silicon, in which all the carbon is in the form of graphite. The last group may be sub-divided into (a) steels formed by a solution of ferrosilicon, and containing bright crystals of the iron silicide, Fe_2Si , (b) steels containing well-formed crystals of the monosilicide, FeSi .

With regard to the mechanical properties of silicon steels, only those containing less than 5 per cent. of silicon have any technical value; these offer a greater resistance to shock after tempering than before, and on this account are particularly useful for the manufacture of springs.

M. A. W.

Preparation of Ammonio-nickel Chloride and Separation of Nickel from other Metals. HANS ALBERT FRASCH (D.R.-P. 146363).—The addition of an excess of ammonia to a solution of nickel chloride produces the known compound $\text{Ni}(\text{NH}_3)_2\text{Cl}_2 \cdot 4\text{NH}_3$, which may be precipitated by sodium or potassium chloride as a violet-blue, very hygroscopic powder, and dried after washing with an ammoniacal solution of an alkali chloride. It separates from warm, slightly ammoniacal water in large, violet, double pyramids. Zinc, copper, &c., remain dissolved in the ammoniacal solution. Iron and manganese are preferably removed by means of calcium carbonate before the addition of ammonia. The same salt is obtained when sodium chloride is added to solutions of other nickel salts, such as the sulphate or chloride.

C. H. D.

Hydrates of Molybdic Acid. II. ARTHUR ROSENHEIM and ISSER DAVIDSOHN (*Zeit. anorg. Chem.*, 1903, 37, 314—325. Compare Rosenheim and Berthelm, *Abstr.*, 1903, ii, 374).—Molybdic acid dihydrate, $\text{MO}_3 \cdot 2\text{H}_2\text{O}$, is conveniently prepared as follows. To a 15 per cent. solution of commercial ammonium paramolybdate, a 20 per cent. solution of nitric acid is added with constant stirring. Ammonium nitrate is then added until the solution contains 10 per cent. of it, and the whole is then sown with a nucleus of molybdic acid dihydrate. After 8 days at 20—25°, an abundant crop of the dihydrate separates.

The solubility of the dihydrate is greatly increased by the addition of ammonium salts; the figures quoted indicate that the dihydrate is not a colloid. On the other hand, a colloidal acid appears to be formed when an aqueous solution of the dihydrate is concentrated under diminished pressure over sulphuric acid at 20°. A vitreous mass

is thus obtained, which dissolves in water to an opalescent solution, which, with electrolytes, gives a precipitate of molybdic acid.

When a solution of molybdic acid dihydrate is concentrated at 40–50°, *α-molybdic acid monohydrate*, $\text{MO}_3 \cdot \text{H}_2\text{O}$, is formed as asbestos-like white needles. It differs from the monohydrate, described as being formed from the dihydrate at 70° (*loc. cit.*), in its more defined crystalline habitus and in the rapidity with which it settles from a suspension in water. Further, it retains its water of crystallisation much more readily than the form previously described (*β*-form).

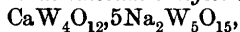
The solubility in water of the *α*-monohydrate was determined at different temperatures. The solubility curves of the *α*-monohydrate and the dihydrate cut one another at 32°, whilst at 60°, the *α*-monohydrate appears to undergo transformation into the *β*-variety. The molecular conductivity of the *α*-monohydrate is almost identical with that of methyl molybdate, whilst the values for the dihydrate are much higher. Solutions of the *α*-monohydrate contain a molybdic acid of a smaller molecular weight than the acid in solutions of the dihydrate. The rate of hydrolysis of methyl acetate by solutions of methyl molybdate was also measured, from which it is concluded that the *α*-monohydrate is a much weaker acid than the dihydrate. The transformation of the various hydrates of molybdic acid into one another is accordingly regarded as involving the formation of intermediate polymerisation products.

Colloidal molybdic acid was obtained by evaporating a solution of the dihydrate at 20°, or, better, by warming a solution of sodium molybdate (1 mol.) and hydrochloric acid (4 mols.). The hydrosol so obtained is readily soluble and, from the solution, electrolytes precipitate the molybdic acid, but whether as hydrogel or hydrosol has not yet been determined. The solutions, previously prepared by other authors according to Graham's method, probably contained no colloidal acids, since electrolytes, when added to them, did not cause a precipitate.

A. McK.

Tungsten Bronzes. EWALD ENGELS (*Zeit. anorg. Chem.*, 1903, 37, 125–151).—The electrolytic preparation of various tungsten bronzes is described. Tungstic acid, prepared from the commercial sodium tungstate, is fused with the calculated amount of the metallic carbonate and the mass then electrolysed.

Sodium barium tungsten bronze, $2\text{BaW}_4\text{O}_{12} \cdot 3\text{Na}_2\text{W}_5\text{O}_{15}$, prepared by a current of 4.5 amperes and 1.6 volts, forms dark blue crystals and, when immersed in water, shows a brilliant red lustre. The *bronze*, $\text{BaW}_4\text{O}_{12} \cdot 5\text{Na}_2\text{W}_3\text{O}_9$, prepared from barium tungstate (1 mol.) and sodium tungstate (3 mols.), forms yellowish-red cubes. *Potassium barium tungsten bronze*, $\text{BaW}_4\text{O}_{12} \cdot 5\text{K}_2\text{W}_4\text{O}_{12}$, forms dark red, quadratic pyramids. *Sodium strontium tungsten bronze*, $\text{SrW}_4\text{O}_{12} \cdot 5\text{Na}_2\text{W}_5\text{O}_{15}$, forms brilliant violet, rhombic or quadratic pyramids. The *bronze*, $\text{SrW}_4\text{O}_{12} \cdot 12\text{Na}_2\text{W}_3\text{O}_9$, crystallises in regular pyramids. *Potassium strontium tungsten bronze*, $\text{SrW}_4\text{O}_{12} \cdot 5\text{K}_2\text{W}_4\text{O}_{12}$, forms red, rhombic or quadratic pyramids. *Sodium calcium tungsten bronze*,



forms violet, rhombic or quadratic pyramids. The *bronze*,

$\text{CaW}_4\text{O}_{12}, 10\text{Na}_2\text{W}_3\text{O}_9$, forms purple cubes or pyramids. *Potassium calcium tungsten bronze*, $\text{CaW}_4\text{O}_{12}, 5\text{K}_2\text{W}_4\text{O}_{12}$, forms glistening, red pyramids. A. McK.

Uranyl Double Nitrates. RICHARD JOS. MEYER and FRITZ WENDEL (*Ber.*, 1903, 36, 4055—4058).—The properties of the double nitrates studied by Meyer (*Abstr.*, 1900, ii, 597; 1901, ii, 510; 1903, ii, 211) rendered it probable that similar compounds would be formed by other metals of high atomic weight.

The double nitrates of uranyl with potassium, ammonium, rubidium, caesium, and thallium crystallise well from nitric acid, and with the exception of the thallium salt, exhibit strong fluorescence. They are decomposed into their components by water, the thallium salt even by moist air. The composition is in all cases represented by the formula $\text{R}'\text{UO}_2(\text{NO}_3)_3$. Attempts to prepare similar salts of sodium and lithium, or of bivalent metals, failed. C. H. D.

Action of Titanic Anhydride on Sodium Carbonate. D. P. SMITH (*Zeit. anorg. Chem.*, 1903, 37, 332—336).—When molecular quantities of sodium carbonate and titanium dioxide are fused together, a homogeneous mass is formed, which gradually loses carbon dioxide on exposure to the atmosphere. In the melted mass, the equilibrium is represented by $\text{Na}_2\text{CO}_3 + \text{TiO}_2 \rightleftharpoons \text{Na}_2\text{TiO}_3 + \text{CO}_2$, and the amount of carbon dioxide in the mass must be very small, since on cooling no carbon dioxide is evolved. When the mixture is heated at 900—1100° in carbon dioxide under atmospheric pressure, the equilibrium is represented by $0.29\text{Na}_2\text{CO}_3 + 0.29\text{TiO}_2 \rightleftharpoons 0.71\text{NaTiO}_3 + x\text{CO}_2$. This equilibrium has been experimentally studied by the author. The interaction between titanium dioxide and potassium carbonate, silica and sodium carbonate, zirconium dioxide and sodium carbonate respectively has also been examined. A. McK.

Bismuth Oxide. W. GUERTLER (*Zeit. anorg. Chem.*, 1903, 37, 222—224).—When melted bismuth oxide was allowed to cool, the mass was observed to glow after crystallisation had begun. The curve of cooling was followed when it was found that during the crystallisation the temperature remained constant at 820° ($\pm 2^\circ$); it then fell to 680° ($\pm 2^\circ$), and then rose to 704° ($\pm 4^\circ$) and finally fell quickly. The transition temperature of the one modification into the other accordingly lies at 704°, a result which was confirmed by the curve of heating. The first modification could not be obtained at the ordinary temperature. A third modification was obtained by heating bismuth oxide in a porcelain crucible; it melts at a higher temperature than the second variety and is more stable; it dissolves in dilute nitric or sulphuric acids less readily than does the second variety. A. McK.

Behaviour of Red Colloidal Gold Solutions towards the Electric Current and towards Electrolytes. J. C. BLAKE (*Amer. J. Sci.*, 1903, [iv], 16, 433—441).—Colloidal gold solution was electrolysed in a U-tube with 0.005 ampere, each electrode just entering the liquid; the gold, after 12 hours, becomes concentrated in a red cloud at the bend of the tube, except for a slight deposit of dark-coloured slime on the anode.

The effect of the addition of various salts in transforming red colloidal gold solutions into blue colloidal gold solutions and in causing subsequent sedimentation has been examined. The stability of red colloidal gold solutions is partly due to the ether present. The influence of various electrolytes on the transformation of red colloidal gold solutions during the passage of the electric current is also described.

A. McK.

Behaviour of Platinum Amalgams with Nitric Acid. NAZARENO TARUGI (*Gazzetta*, 1903, 33, [ii], 171—186).—The method proposed by Knoevenagel and Ebber (*Abstr.*, 1902, ii, 697) for the separation of the metals of the second group, is not only less simple than methods previously in use but contains fresh sources of error. In particular, the proposed separation of bismuth, platinum, and gold is by no means complete, whilst arsenates become reduced to arsenites, which hinder the reduction of gold and platinum salts by the hydrazine. Further, in a mixture of finely-divided metals, such as is obtained by reduction from solutions of their salts, the individual metals do not retain the distinctive chemical properties which they possess in the free, unmixed condition. Especially is this so when mercury is present, as then amalgams are formed, the properties of which render inapplicable the ordinary method of separating the metals by means of acids. Thus, from a mixture containing 4.64 per cent. of platinum and 95.35 of mercury, nitric acid dissolves the whole of the platinum; as the percentage of platinum present increases, the proportion of the total amount dissolved by the acid diminishes, whilst the proportion of mercury dissolved decreases from 99 per cent. in a mixture of 91.11 parts of mercury and 8.88 of platinum to zero for a mixture of 17.02 per cent. of mercury with 82.97 of platinum.

Microscopic examination confirms the fact that amalgams are formed during the simultaneous reduction of platinum and mercury from solutions of their salts.

With a mixture of gold and mercury salts in solution, however, reduction by hydrazine does not lead to the formation of amalgams.

T. H. P.

Platinum Phosphorus Halogen Compounds and their Derivatives. I. ARTHUR ROSENHEIM and WILLY LOWENSTAMM (*Zeit. anorg. Chem.*, 1903, 37, 394—406).—Trichlorophosphorusplatochloride, prepared by the action of phosphorus pentachloride on platinum at 250°, may be represented as $\text{PCl}_3\cdot\text{PtCl}_2$ or $\text{Pt}(\text{PCl}_3)\text{Cl}_2$, whilst ditrichlorophosphorusplatochloride is $(\text{PCl}_3)_2\cdot\text{PtCl}_2$ or $\text{Pt}(\text{PCl}_3)_2\text{Cl}_2$. The research was undertaken to decide whether those compounds are analogous to the platamines of Werner, of which the compound $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ may be taken as a type. Molecular weight determinations with the two chlorides under consideration led to no result, since the substances decomposed in boiling solvents and were too insoluble in cold solvents to permit of cryoscopic observations being made with them. Successful determinations could, however, be made with the ethers, which are easily obtainable from the chlorides.

Ethyl phosphite platochloride, $\text{P}(\text{OEt})_3\cdot\text{PtCl}_2$, forms dark yellow prisms. *Dimethyl phosphite platochloride*, $[\text{P}(\text{OMe})_3]_2\cdot\text{PtCl}_2$, crystal-

lises in prismatic needles. The analogy with Werner's platosamines is shown, and evidence is also submitted to indicate that phosphorus in these compounds is tervalent. By the action of halogen on compounds of tervalent phosphorus and bivalent platinum, compounds are obtained which contain quadrivalent platinum and quinquevalent phosphorus. When chlorine is passed into a benzene solution of ethyl phosphite platochloride, reddish-yellow crystals of *triethyl phosphate platinic chloride*, $\text{PtCl}_4 \cdot \text{PO}(\text{OEt})_3$, separate. *Triethyl phosphate platinic dibromochloride*, $\text{PtCl}_2\text{Br}_2 \cdot \text{PO}(\text{OEt})_3$, prepared by the action of dry bromine on a benzene solution of ethyl phosphite platochloride, separates in purple, deliquescent prisms.

Platinic chloride, prepared by heating chloroplatinic acid in a current of chlorine at 275° , acts only on the esters of quinquevalent phosphorus and not on those of tervalent phosphorus; with ethyl phosphate, it interacts to form triethyl phosphate platinichloride, whilst it does not act on ethyl phosphite. Platinous chloride, on the other hand, reacts with esters of phosphorous acid, but not with esters of phosphoric acid.

A. McK.

Action of a Mixture of Oxygen and Hydrochloric Acid on some Metals. CAMILLE MATIGNON (*Compt. rend.*, 1903, 137, 1051—1052. Compare Abstr., 1902, ii, 556).—In addition to gold, platinum, and tellurium, the author finds that all the metals of the platinum series are chlorinated by a mixture of air and hydrochloric acid. Palladium is attacked in the cold, 2.6 grams of the metal lost 0.23 gram in several weeks, and from the solution the chloride PdCl_2 was isolated. Spongy ruthenium is very slowly attacked at the ordinary temperature, but in a sealed tube at 125° the chlorination is complete in a few hours, crystals of chlororuthenic acid being formed. Iridium, free from iron, is not attacked in the cold, but after heating at 150° with hydrochloric acid in a sealed tube containing oxygen for 6—8 hours, the solution reacts with the chlorides of ammonium, potassium, or caesium to give the corresponding coloured iridiochlorides. Rhodium turnings are not attacked in the cold, but at 150° there is a slow reaction, the solution assuming the rose-colour characteristic of rhodium salts, whilst at 200° the solution is more rapid, as much as one gram of rhodium being dissolved in one experiment. Spongy osmium passes slowly into solution at 150° , the solution assuming the yellowish-green colour characteristic of osmium salts.

M. A. W.

Iridium Sesquiselenide. CAMILLE CHABRIÉ and A. BOUCHONNET (*Compt. rend.*, 1903, 137, 1059—1061).—Iridium sesquiselenide, Ir_2Se_3 , precipitated by hydrogen selenide from a hot solution of iridium sesquichloride, is a non-crystalline, shining black powder, not attacked by ordinary nitric acid, even on warming, slightly decomposed by fuming nitric acid in sealed tubes at 250° , and slowly dissolved by aqua regia. When iridium and selenium are heated to redness in sealed tubes for several hours, a black, confusedly crystalline mass is obtained, which differs from the preceding compound by the greater resistance it offers to the action of reagents; it is not attacked by

aqua regia, bromine water, or a mixture of alkali nitrates and chlorates, and it can be fused with lead fluoride without undergoing decomposition.

M. A. W.

Mineralogical Chemistry.

Sartorite from the Binnenthal, Switzerland. WILLIAM J. LEWIS (*Min. Mag.*, 1903, 13, *Proc.* xxxiv).—A large isolated crystal, measuring $4 \times 1 \times \frac{1}{3}$ inch, of a sulpharsenite of lead proved, on analysis by H. JACKSON, to be sartorite. The results obtained were: Pb, 42.93; As, 31.11; S, 25.32. L. J. S.

Swedish Hausmannites. ALEXANDRE GORGEU (*Bull. Soc. chim.*, 1903, [iii], 29, 1109—1111. Compare *Abstr.*, 1894, 19, 99).—Three specimens of Swedish hausmannite were found to contain small quantities of the bivalent metals, zinc, magnesium, calcium, and barium. These constituents are regarded not as mechanical impurities, but as existing in combination with the manganese sesquioxide, and partially replacing manganous oxide in the mineral (compare this vol., ii, 126). T. A. H.

Turgite-ores in Russia. J. SAMOJLOFF (*Zeit. prakt. Geol.*, 1903, 11, 301—302. Compare *Abstr.*, 1901, ii, 605).—Turgite (= turjite), which is to be regarded as a definite mineral species ($2\text{Fe}_2\text{O}_3, \text{H}_2\text{O}$), is of some importance in Russia as an ore of iron; its occurrence is noted at several localities in the Northern (river Turja, &c.) and Southern Urals, and in Central Russia. Analysis of material from Wladimirowka, gov. Tula, gave:

| Fe_2O_3 . | SiO_2 . | Al_2O_3 . | P_2O_5 . | H_2O . | Total. |
|---------------------------|------------------|---------------------------|--------------------------|------------------------|--------|
| 87.93 | 2.12 | 1.60 | 1.57 | 6.52 | 99.74 |

L. J. S.

Refractive Indices of Pyromorphite, Mimetite, and Vanadinite. HERBERT L. BOWMAN (*Min. Mag.*, 1903, 13, 324—329).—Detailed determinations of the refractive indices for light of three colours are given of the minerals of this group. The substitution of arsenic for phosphorus and of vanadium for arsenic in each case causes an increase in the refractive indices. The following values obtained for red (C) light may be quoted:

| | ϵ . | ω . |
|---|--------------|------------|
| I. Pyromorphite (Braubach, Nassau) | 2.042 | 2.0504 |
| II. Mimetite (Wheal Alfred, Cornwall ?) ... | 2.1178 | 2.1344 |
| III. Mimetite (Tintic district, Utah) | 2.1178 | 2.1326 |
| IV. Endlichite (Hillsboro', New Mexico) ... | 2.292 | 2.341 |
| V. Vanadinite (Tucson, Arizona) | 2.299 | 2.354 |

The pale green mimetite (II) from Cornwall (?) contained only a trace of phosphoric acid, and the white mimetite (III) from Utah contained none. The pale liver-coloured pyromorphite (I) from Nassau, gave, on analysis :

| PbO. | P ₂ O ₅ . | As ₂ O ₅ . | Cl | F. | Fe, Ba, Ca. | Total (less O for Cl). |
|-------|---------------------------------|----------------------------------|------|-----|-------------|---------------------------|
| 81.12 | 16.51 | nil | 2.71 | nil | traces | 99.73 |

L. J. S.

Rösslerite and Wapplerite. AUGUST B. DE SCHULTEN (*Bull. Soc. franç. Min.*, 1903, 26, 99—103).—Attempts to prepare wapplerite [$\text{H}(\text{Ca}, \text{Mg})\text{AsO}_4 \cdot 3\frac{1}{2}\text{H}_2\text{O}$] were without success, and resulted in the formation of crystals of rösslerite ($\text{HMgAsO}_4 \cdot 7\text{H}_2\text{O}$; sp. gr. 1.943), or of rösslerite together with pharmacolite. The existence of wapplerite is therefore doubted; it is suggested that the material analysed for wapplerite was a mixture of magnesium and calcium arsenates, whilst the crystallographic determinations were made on rösslerite.

L. J. S.

Wollastonite [and Garnet] from Mexico. HENRY F. COLLINS (*Min. Mag.*, 1903, 13, 356—362).—A description is given of a large boss of coarsely crystallised wollastonite, of presumably igneous origin, in which are the workings of the Santa Fé mine, State of Chiapas. Near the outskirts of the mass, the wollastonite is found as large crystals, frequently altered to opal, and is much intermixed with garnet, opal, bornite, siegenite (*Abstr.*, 1902, ii, 460), enargite, &c. The rhombic dodecahedra of garnet vary in colour from olive-green to resin-yellow and reddish-brown; analysis of green crystals gave I, of brown, II, and of both green and brown, III.

| | SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | CaO. | MgO. | Total. | Sp. gr. |
|------|--------------------|----------------------------------|----------------------------------|-------|------|--------|---------|
| I. | 36.10 | — | 19.30 | — | — | — | — |
| II. | 36.48 | — | 19.50 | — | — | — | — |
| III. | 36.35 | 12.37 | 19.43 | 33.33 | 0.40 | 101.88 | 3.89 |

L. J. S.

Composition of Glauconite and Greenalite. FRANK W. CLARKE (*Monogr. U.S. Geol. Survey*, 1903, 43, 243—247).—From Glinka's analyses (*Abstr.*, 1899, ii, 112), the formula of ideally pure glauconite is deduced as $\text{KFe}'''\text{Si}_2\text{O}_6 \cdot \text{H}_2\text{O}$. Analyses by G. Steiger of the portions soluble in hydrochloric acid of the greenalite-rocks of Minnesota are given under I—III; the insoluble portion consists mainly of quartz. The second of these approximates to the simple formula $\text{Fe}_2''(\text{Fe}'', \text{Mg})_3(\text{SiO}_4)_3 \cdot 3\text{H}_2\text{O}$; the first also gives an orthosilicate ratio, but the third approximates to a metasilicate.

| | SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | MgO. | CaO. | H ₂ O. | CO ₂ . | Total. |
|------|--------------------|----------------------------------|----------------------------------|-------|------|------|-------------------|-------------------|--------|
| I. | 13.45 | 0.37 | 15.00 | 10.28 | 2.33 | 0.28 | 4.17 | 2.04 | 47.92 |
| II. | 19.30 | 0.61 | 13.83 | 17.57 | 3.22 | — | 5.74 | — | 60.27 |
| III. | 33.11 | 0.56 | 6.44 | 30.93 | 5.35 | — | 6.13 | — | 82.52 |

CHARLES K. LEITH (*ibid.*, 1—316) gives the name *greenalite* to green granules with the above composition, which occur abundantly as a constituent of the sedimentary rocks in the Mesabi iron-bearing district of Minnesota. The mineral closely resembles glauconite in appearance, but differs from it in containing no potassium. By the alteration of the greenalite, ferruginous cherts are formed, as well as immense deposits of iron ore. L. J. S.

Bakerite (a New Borosilicate of Calcium) and Howlite from California. WILLIAM B. GILES (*Min. Mag.*, 1903, 13, 353—355).—Bakerite occurs as veins and nodules of considerable size in the mines of the Borax Consolidated Company in San Bernardino Co., California. In appearance, the white, amorphous masses resemble unglazed porcelain, fine white marble, or pandermite; sometimes the mineral has a faint sea-green tint. H. $4\frac{1}{2}$; sp. gr. 2.73. The mineral is readily soluble in warm dilute hydrochloric acid. The following analyses of I, white material, and II, of material with a green tinge, give the formula $8\text{CaO}, 5\text{B}_2\text{O}_3, 6\text{SiO}_2, 6\text{H}_2\text{O}$, showing the mineral to be distinct from danburite, datolite, and howlite, the previously known borosilicates of calcium.

| | B_2O_3 . | CaO . | SiO_2 . | H_2O . | $\text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3$. | $\text{Na}_2\text{O}, \text{MgO}$. | Total. |
|------|--------------------------|----------------|------------------|------------------------|--|-------------------------------------|--------|
| I. | 27.74 | 34.88 | 28.45 | 8.30 | 0.63 | — | 100.00 |
| II. | 26.85 | 35.22 | 28.05 | 8.66 | 1.22 | — | 100.00 |
| III. | 44.38 | 28.45 | 15.50 | 11.58 | — | 0.09 | 100.00 |
| IV. | 43.78 | 28.44 | 15.33 | 11.39 | — | 1.06 | 100.00 |

Howlite, colemanite, natroborocalcite, and pandermite also occur at the same locality. The howlite ($4\text{CaO}, 5\text{B}_2\text{O}_3, 2\text{SiO}_2, 5\text{H}_2\text{O}$) occurs in large amount; soft, scaly, white material gave analysis III, and hard, rock-like, white masses gave the results under IV. L. J. S.

Volcanic Ash from Mont Pelée, Martinique. ARTHUR B. GRIFFITHS (*Bull. Soc. chim.*, 1903, iii, 29, 1117).—The ash was microcrystalline, had sp. gr. 2.7211 and contained 3.24 per cent. of magnetic matter. The material, dried at 120° , gave on analysis:

| SiO_2 . | Al_2O_3 . | CaO . | Fe_2O_3 . | FeO . | MnO . | MgO . |
|------------------------|---------------------------|------------------|---------------------------|--------------------------|----------------|----------------|
| 55.01 | 20.50 | 9.00 | 3.20 | 4.86 | 0.25 | 3.06 |
| K_2O . | Na_2O . | TiO_2 . | SO_3 . | P_2O_5 . | Cl. | Total. |
| 0.65 | 2.01 | 0.68 | 0.42 | 0.20 | 0.16 | 100.00 |

Together with traces of copper, nickel, and lithium.

T. A. H.

Meteoric Iron. FLORIS OSMOND and G. CARTAUD (*Compt. rend.*, 1903, 137, 1057—1059. Compare Abstr., 1902, ii, 400).—Meteoric iron, whether it has passed through the liquid state or been formed by the reduction of the chlorides, consists of homogeneous solid solutions of γ -iron and β -nickel. The solution, on cooling, deposits kamacite when the proportion of nickel is below 13 per cent., ténite when the

proportion of nickel is above 44 per cent., or a mixture of kamacite and t  nite when the solution contains proportion of nickel intermediate between these two values. From a solution containing 30 per cent. of nickel, plessite, which may be regarded as the eutectic mixture of kamacite and t  nite, is deposited.

M. A. W.

Physiological Chemistry.

Quantity of Fat contained in Human Blood and Some Organs. THEODOR RUMPF, H. DENNSTEDT, and A. GRONOVER (*Chem. Centr.*, 1903, ii, 1253—1254; from *Virchow's Archiv*, 174, 163—193). —The blood of two still-born children was found to contain 0.057 and 0.007 per cent. of fat respectively, and since these quantities could not have been affected by previous nutrition they were regarded as normal. In cases of severe diabetes (coma), a slight increase of the content of fat is only occasionally observed, although in six cases the blood contained 0.015—0.124 per cent. In cases of arteriosclerosis, the fat increased regularly by small quantities and amounted to 0.11—0.183 per cent., but with simultaneous alcoholism the percentages were only 0.05 and 0.032. The largest quantity of fat, 0.335 per cent., was found in a case of leucæmia; in phthisis and in cirrhosis of the kidneys, 0.02 and 0.012—0.037 per cent. were observed respectively.

The hearts of the still-born children contained 12.93 and 15.84 parts of fat per 100 parts of dry substance. The higher limit in normal cases of this kind reaches 16 per cent. and corresponds with a content of 1 gram of nitrogen to 1.2—1.3 of fat. In two cases of arteriosclerosis, the hearts contained 52.61 and 59.32 per cent. respectively, and a case of leucæmia gave a percentage of 57.8. In diabetes, the fat reached 25.3—40.54 with the exception of one case of 16.1 per cent.; in nephritis 40.2 per cent. Constant results were not obtained in cases of anæmia and carcinoma.

The peripheral muscular system contains, in a normal state, 15.7 per cent. of fat, but 45.49—47.6 was found in degenerated muscles (multiple neuritis), corresponding with 1 gram of nitrogen to 2.3 of fat.

The livers of the still-born children contained 15.52 and 17 per cent. of fat respectively. In cases of cirrhosis of the kidneys with fatty degeneration of the liver, alcoholism, and tuberculosis, 34.6, 47.0, and 56.6 per cent. of fat were found respectively. The first stages of alcoholism are attended by increase in the amount of fat contained in the liver, but as the process of degeneration proceeds the fat gradually decreases to the normal amount and less. The kidneys of the still-born children contained 19.2 and 22.82 per cent. of fat respectively. In cases of pernicious anæmia, congestion of the kidneys, and cirrhosis

of the kidneys, the quantity of fat increased to 34.3, 32, and 28 per cent. respectively.

No general conclusions could be drawn from the results of determinations of the fat in the spleen.

The solid fatty acids isolated from human fat have a low refractive index, and hence contain not only palmitic and stearic acids, but probably also myristic or lauric acid.

E. W. W.

Formation of Oxalic Acid in the Animal Organism.

ADOLFO MONTUORI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1903, [iii], 9, 202—207).—Wiener (Abstr., 1902, ii, 338) has shown that, especially in birds, feeding with (among other substances) glycerol and propionic, lactic, pyruvic, hydraerylic, tartronic, malonic, mesoxalic, or β -hydroxybutyric acid, combined with simultaneous hypodermic injection of urea, determines a considerable increase in the secretion of uric acid. This he explains by supposing that the 3-carbon atom chain contained in the molecule of each of these compounds is capable of combining with two ureic residues to form uric acid. Now the author has previously shown (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1901) that the introduction of oxalic acid into the animal organism also brings about the production of uric acid, and the present investigations, made with malonic, tartronic, lactic, β -hydroxybutyric, and citric acids and glycerol, were carried out with the object of discovering whether the feeding of dogs with these substances caused the formation of oxalic acid in the organism. With malonic, tartronic, and citric acids, positive results were obtained. With lactic acid, oxalic acid sometimes appeared in the urine, but never in large quantities; with birds, this acid may act differently. With β -hydroxybutyric acid, the gastro-enteric disturbances produced by even small proportions of the acid rendered the results valueless. Glycerol gave negative results. On administering sodium citrate internally to a dog, and at the same time injecting urea solution, the secretion of uric acid was increased.

T. H. P.

Poisoning by Barium Salts. Presence of Barium in the Urine and the Absorption and Elimination of the Metal. LUIGI SANTI (*Gazzetta*, 1903, 33, ii, 202—216).—Barium was detected in considerable quantities in the urine and blood of a dog which had been poisoned by barium chloride, although in both cases soluble sulphates were simultaneously present in these fluids. It is shown experimentally that barium sulphate is dissolved to a considerable extent by a solution of sodium hydrogen carbonate, and that on adding a small quantity of sodium sulphate to a solution of the latter containing a few drops of barium chloride solution, no precipitate is formed. On boiling, barium carbonate is precipitated, and then on adding an acid the carbonate is dissolved, but is almost immediately reprecipitated as sulphate.

Dissolved carbon dioxide can act in a similar manner in preventing the precipitation of barium in presence of soluble sulphates. It is suggested that the presence of barium in the blood and urine in cases of barium poisoning is due to the sodium hydrogen carbonate in the

former and the carbon dioxide dissolved in the latter. The other salts normally contained in these liquids have no power to render barium sulphate soluble.

W. A. D.

Chemistry of Vegetable Physiology and Agriculture.

Methane Fermentation and the Ferment by which it is Produced. PIERRE MAZE (*Compt. rend.*, 1903, 137, 887—889).—A ferment which produces marsh gas was obtained from dead leaves. When the ferment was destroyed by heating at 60°, it was found that the mixed culture contained butyric and acetic ferments, whilst in presence of the methane ferment no acetic or butyric acid was detected. The conclusion is drawn that the methane ferment is fed at the expense of the products furnished by the butyric ferments. In support of this view, it was found that the methane ferment liberates marsh gas in absence of carbohydrates. The gaseous product consisted of marsh gas (81) and carbon dioxide (19 per cent.); but in some cases as much as 90 per cent. of marsh gas was found.

The ferment is provisionally termed *pseudo-sarcine*.

Pure cultivations were made, but all attempts to obtain fermentation with them failed.

N. H. J. M.

Fermentation of Citric Acid as a Cause of Disease in Currant Wine. W. SEIFERT (*Chem. Centr.*, 1903, ii, 1286; from *Zeit. landw. Vers. Wes. Oest.*, 6, 738—747).—Currant wine which has been fermented is occasionally attacked by a disease which results in rendering the wine acid, turbid, and of a paler shade of colour; its taste also becomes harsh. The precipitate formed in these cases was found not only to contain yeast, but also numerous bacteria in the form of small rods. Attempts to isolate a pure culture failed, but by means of the mud, malic acid was converted into lactic acid, and citric acid was fermented, forming carbon dioxide, acetic acid, and alcohol. The latter process probably accounts for the disease of the wine.

Grape wines also contain micro-organisms which are able to ferment citric acid, and hence it is unwise to add this acid to such wines.

E. W. W.

Uric Acid Bacterium. CELSO ULPANI (*Gazzetta*, 1903, 33, ii, 93—98).—It has been previously shown that, under certain conditions, a solution of uric acid undergoes a definite form of fermentation, and the author has now isolated the organism to which this is due by taking the fresh excreta of fowls and allowing them to remain in water for several days. The bacillus is motile, and appears in coccus forms which resist decolorisation by Gram's method. A clear saturated aqueous solution of uric acid containing small quantities of mineral matter, when inoculated with the bacterium, becomes turbid after 24 hours and whitish after 3 days, and after 4 days no longer

gives the slightest trace of murexide reaction. Destruction of the uric acid takes place between the temperature limits, 29—42°, the optimum being 37°. The products of the action are carbamide and carbon dioxide.

T. H. P.

Chemical Equation of the Fermentation of Uric Acid. M. CINGOLANI (*Gazzetta*, 1903, 33, [ii], 98—125. See preceding abstract).—The author has determined quantitatively the products formed in the decomposition of uric acid by the uric acid bacterium, and finds the reaction to be expressed by the equation: $C_5H_4O_3N_4 + 2H_2O + 3O = 2CO(NH_2)_2 + 3CO_2$. The methods employed, which are fully described, include a biological method of estimating carbamide by converting it into ammonium carbonate by means of the carbamide bacterium.

T. H. P.

Decomposition of Yeast Nucleic Acid by Bacteria. II and III. ALFRED SCHITTENHELM and F. SCHROTER (*Zeit. physiol. Chem.*, 1903, 40, 62—69, 70—80. Compare Abstr., 1903, ii, 679; and Iwanoff, *ibid.*, ii, 678).—The following organisms have been employed: *Bacterium coli*, *Staphylococcus pyogenes albus*, and a bacterial mixture from fresh faeces, the nutrient medium being Uschinsky's solution with and without sodium aspartate and ammonium lactate. The different organisms behave somewhat differently, and even the same organism can give different results with different media. Certain species destroy the nucleic acid yielding purine bases, others even decompose these bases. They do not all decompose the acids at the same rate, and the rate with a single species appears to be proportional to the number of active organisms present.

The gases evolved in the decomposition of yeast nucleic acid by bacteria have been examined. The mixed gases were found to consist of carbon dioxide, oxygen, nitrogen, and, in one case, hydrogen and methane.

When glycerol is present, the percentage of carbon dioxide is much higher.

J. J. S.

Denitrification in Soil. II. GASPARE AMPOLA and CELSO ULPANI (*Gazzetta*, 1903, 33, [ii], 125—129. Compare Abstr., 1901, ii, 524).—The cultivation experiments previously described (*loc. cit.*) were continued during last season, and confirm the results formerly obtained. The conclusions arrived at are: (1) under ordinary conditions, calcium nitrate, the natural product of nitrification, is but slightly attacked by denitrifying bacteria. To avoid loss of nitrogen, fresh stable manure, rich in straw, should not be applied to the ground during the period of nitrification. (2) In order that sodium nitrate may be employed to the best advantage, it must be applied when the stable manure in the soil has reached its state of maximum maturation.

T. H. P.

Influence of the Assimilable Nitrogen of the Soil on the Action of Nodule Bacteria. FRIEDRICH NOBBE and L. RICHTER (*Landw. Versuchs-Stat.*, 1903, 59, 167—174).—*Vicia villosa* was grown

in pots containing 4.5 kilos. of sand and 0.6 kilo. of garden soil under the following conditions: (1) without nitrate; (2) with 0.5 gram, and (3) with 1 gram of nitrogen as nitrate per pot. In one set, the pots were inoculated with a pure cultivation of *Vicia* nodule bacteria, and there was a second set without inoculation. The results showed that whilst in both sets the nitrate increased the growth according to the amount applied, the effect of inoculation (as measured by deducting the production in the pots without inoculation from that of the corresponding inoculated pots) diminished under the influence of nitrates.

In another set of experiments, the same plants were grown in a mixture of sand (4.0 kilos.) and garden soil (2.5 kilos.). During the first period of growth (beginning of June to the middle of July), the inoculated plants were less advanced and more restricted in growth than those which were not inoculated. By September 2nd, the growth in the two sets was about equal, and by the end of September the inoculated plants showed considerably more growth and contained much more nitrogen than the others.

N. H. J. M.

After Effect of the Inoculation of Papilionaceous Plants on other Plants. FRIEDRICH NOBBE and L. RICHTER (*Landw. Versuchs.-Stat.*, 1903, 59, 175—177).—The results of experiments with oats grown in the pots of sand mixed with soil previously used for *Vicia villosa* (preceding abstract) showed that a greater yield of oats was obtained in the pots inoculated for *Vicia* than in those which had not been inoculated. The greater yields are accounted for by the larger root residues of the inoculated plants.

N. H. J. M.

Influence of External Media on the Mineral Constituents of Plants. ALEXANDRE HÉBERT and GEORGES TRUFFAUT (*Bull. Soc. chim.*, 1903, [iii], 29, 1235—1239. Compare Abstr., 1902, ii, 346, 523; 1903, ii, 172, 233, 505, and 607).—Comparative tables of the mineral constituents of a number of different plants, grown with and without manures, are given, and attention is directed to the fact that the table shows that the application of manures in agriculture does not induce any change in the character of the mineral constituents of a plant, although it may affect the proportion in which particular constituents occur, and hence that merely the rate of plant assimilation, but not its nature, is influenced by manures.

T. A. H.

Influence of External Media on the Composition of the Organic Matter of Plants. ALEXANDRE HÉBERT and EUGÈNE CHARABOT (*Compt. rend.*, 1903, 137, 799—801).—The amounts of carbon, hydrogen, and nitrogen were determined in the upper parts and in the roots of the peppermint plants grown under conditions previously described (Abstr., 1903, ii, 607). The percentage results were very similar, notwithstanding the diversity of the salts applied as manure.

N. H. J. M.

What is the Compound contained in certain Plant Juices which is able to liberate Iodine from Potassium Iodide? KEIJIRŌ ASŌ (*Chem. Centr.*, 1903, ii, 1249; from *Beiheft. Bot. Centr.*, 15, 208—214).—Kastle and Loewenhardt's theory that the oxidising agents contained in plant juices are organic peroxides is not in accordance with the author's observations, and no decisive proof has been advanced that the liberation of iodine from potassium iodide is due to the presence of such peroxides. Ordinary oxydase does not liberate iodine from the iodide, and there does not appear to be any connection between the guaiacum and the iodine reactions. The liberation of iodine in the case of buds of *Sagittaria* has been found to be due to the presence of nitrites. Many plants contain certain benzene compounds which interfere with the Griess test for nitrites.

E. W. W.

Lecithins prepared from Plants. I. ERNST SCHULZE and ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1903, 40, 101—119).—Largely a *résumé* of previous work (compare Abstr., 1889, 645; 1891, 1541; 1893, ii, 185; 1894, ii, 155, 402; 1895, ii, 96). The lecithins have been obtained not merely by extraction with ether but also with alcohol at 50—55°. The crude lecithin contains a substance which is sparingly soluble in alcohol. This is not a pure compound, as the product obtained from different seeds varies in composition and the composition is largely altered by extraction with alcohol. The substance, on hydrolysis with baryta, yields choline, glycerophosphoric acid, and fatty acids.

The fate of lecithins in the germinating seed is also discussed (Schulze and Maxwell, 1891, 1541; also Iwanoff, *ibid.*, 1903, ii, 94; and Zaleski, *ibid.*, ii, 94).

J. J. S.

The Sap of Asclepias Syriaca. J. MAREK (*J. pr. Chem.*, 1903, [ii], 68, 449—463. Compare this vol., ii, 73).—On recrystallisation from a mixture of ether and alcohol, that part of the sap residue which is only slightly soluble in 95 per cent. alcohol yields an *acetate*, $C_{30}H_{49} \cdot OAc$, which crystallises in long, colourless prisms and melts at 239—240°. On hydrolysis with alcoholic potassium hydroxide, it yields potassium acetate and a *hydroxy-compound*, $C_{30}H_{50}O$, which crystallises in clusters of long, thin, colourless prisms and melts at 192—193°. It gives a yellow to carmine coloration with Liebermann's reagent, and when boiled with dilute nitric acid yields a yellow *product* which dissolves in alkalis to a yellow solution. With benzoic chloride in benzene solution, the hydroxy-compound forms a *benzoate*, $C_{30}H_{49} \cdot OBz$, which crystallises in colourless prisms, melts at 229—230°, and is soluble in benzene but only slightly so in alcohol or ether. The ether-alcoholic mother liquors from the purification of the acetate contain a *butyrate*, which separates as a yellow, transparent resin, melts at 71—75°, and on hydrolysis yields potassium butyrate, a small amount of potassium acetate, and a *hydroxy-compound* which loses weight on drying; the product, after 44 hours, melts at 87—90° and gives yellow, through red, to green colorations with Liebermann's reagent.

On treatment of the sap with water and repeated extraction of the

insoluble part with alcohol, a white precipitate is obtained on cooling the alcoholic extract. This precipitate, on crystallisation from ether, yields two substances. The one, $C_{34}H_{56}O_3$ or $C_{35}H_{58}O_3$, is a yellow, amorphous, transparent substance and melts at $79-83^\circ$. The other substance crystallises from ether in white, cauliflower-like aggregates, melts at $215-216^\circ$, and on hydrolysis with alcoholic potassium hydroxide yields potassium butyrate and a hydroxy-derivative, $C_{28}H_{46}O$, which crystallises in glistening, delicate needles, melts at $180-181^\circ$, is insoluble in water, soluble in alcohol, and easily so in other organic solvents; with Liebermann's reagent, it gives an orange-red coloration, which fades after a time. When boiled with dilute nitric acid, it yields an orange-yellow nitro-compound. The acetate, $C_{28}H_{45}\cdot OAc$, resembles the butyrate in its crystalline form and melts at $201-202^\circ$; the benzoate, $C_{28}H_{45}\cdot OBz$, forms colourless, prismatic crystals, melts at $195-196^\circ$, and is hydrolysed with formation of the hydroxy-derivative melting at $180-181^\circ$. In one experiment, the hydroxy-compound obtained melted at $162-163^\circ$.
G. Y.

Production and Distribution of some Organic Substances in Citrus Madurensis. EUGÈNE CHARABOT and G. LALOUÉ (*Compt. rend.*, 1903, 137, 996—998. Compare Abstr., 1903, i, 47; ii, 568).—The stems of *Citrus madurensis* contained less water than the leaves during the early periods of growth. The acidity (volatile acids) is greater in the young plants than when the plants are more advanced; the actual amount of volatile acids, however, increases. Odoriferous compounds are formed most abundantly when the leaves are young, and are more abundant in the leaves than in the stems. Later on, there is a renewal of methyl methylantranilate in the leaves; a slighter increase is observed in the stems. The amount of terpenes in the leaves diminishes continuously, but the loss is less than the gain in the stems.
N. H. J. M.

Medicinal and Nut-bearing Plants of Brazil. THEODORE PECKOLT (*Chem. Centr.*, 1903, ii, 1334—1337; from *Ber. Deutsch. Pharm. Ges.*, 13, 21—38).—The abstract contains a detailed description of the quantitative composition of the following plants: *Rubachia glomerata*, *Aulomyrcia ramulosa*, *Myrcia elongata*, *Phyllocalyx tomentosus*, *Stenocalyx Michellii*, *Stenocalyx brasiliensis*, *Myrciaria cauliflora*, *Myrciaria plicata costata*, *Jambosa vulgaris*, *Psidium guayavi*, *Psidium araca*, *Psidium variabile*, *Psidium acutangulum*, *Pseudocaryophyllus sericeus*, *Campomanesia reticulata*, *Carica papaya*, and *Jacaratia dodecaphylla*.
E. W. W.

Influence of Calcium Carbonate in the Decomposition of Organic Matter. P. KOSSOWITSCH and J. TRETJAKOFF (*Bied. Centr.*, 1903, 32, 805—812; from *J. exper. Landw.*, 1902, 3, 450—484).—Oak leaves and hay (representing the herbage of the steppes) were kept for several weeks in a moist condition both without and with calcium carbonate. It was found that in absence of calcium carbonate about 50 per cent. more carbon dioxide was liberated than when

calcium carbonate was present. The materials were inoculated with a little soil. Under natural conditions, the effect of calcium carbonate in the soil is to retain humus and to hinder the washing out of alumina and ferric oxide. A distinction must, however, be made between an excess of calcium carbonate in the soil, and small amounts insufficient to neutralise all the humic acid.

N. H. J. M.

Chemical Changes in Cheese-ripening as Affected by Different Conditions. LUCIUS L. VAN SLYKE and EDWIN B. HART (*Amer. Chem. J.*, 1904, 31, 45—61. Compare Abstr., 1903, i, 215 ; ii, 388, 389, 609).—A study has been made of the influence of time, temperature, moisture, size, salt, rennet, and acid on the chemical changes which take place in the nitrogenous compounds during the ripening of cheese. The results show that the formation of nitrogenous compounds soluble in water increases with the age of the cheese, with increase of temperature, with the amount of moisture present, with the size of the cheese, with the quantity of salt present, and with the proportion of rennet employed. The presence of acid appears to be essential to the production of soluble nitrogenous compounds, but the effect of varying quantities of acid on the chemical changes has not yet been fully investigated. Paranuclein, caseoses, and peptones are present in the early stages, show a tendency to increase for a time, and afterwards decrease, whilst amino-compounds and ammonia accumulate in increasing quantities under all conditions that favour their formation. The changes in the nitrogenous compounds take place much more rapidly in the earlier than in the later stages.

E. G.

Estimation of Assimilable Plant Food by Extracting the Soil with very Dilute Acids. HENRIK G. SÖDERBAUM (*Bied. Centr.*, 1903, 32, 795—798 ; from *Kungl. Landtbr.-akad. handl. tidskr.*, 1903, 103—106).—Pot experiments are described in which barley was grown in loamy soil and in humus soil previously extracted for 48 hours with 2 per cent. hydrochloric acid. The series also included the same soils in their natural condition. The different pots received calcium carbonate, phosphoric acid, potash, and nitrogen, both singly and together.

The extracted loamy soil, alone and with addition of phosphoric acid (as calcium salt), potash, and nitrogen, gave no crops at all, but addition of calcium carbonate alone produced growth amounting to 56 per cent. of the growth in the unextracted soil, and when phosphoric acid and nitrogen (but no potash) were supplied in addition to calcium carbonate, the yield was a little higher than that of the unextracted soil.

The results indicate that extraction with 2 per cent. hydrochloric acid did not cause a distinct want of assimilable phosphoric acid and potash, and that the amount of nitrogen was not sufficiently reduced to prevent the plants from ripening. The assimilable constituents of the soil were therefore only partially extracted.

N. H. J. M.

Influence of the Relative Amounts of Calcium and Magnesium in the Soil on the Crop Yield. OSCAR LOEW (*Chem. Zeit.*, 1903, 100, 1225—1226. Compare Abstr., 1902, ii, 622).—The result of Gössel's water-culture experiments (*Chem. Zeit.*, 1903, 952), in which it was found that the greatest yield was obtained when the relation $\text{CaO} : \text{MgO} = 0.4 : 1$, is attributed to the employment of dipotassium phosphate, which would tend to eliminate the injurious effect of an excess of magnesium (compare Loew, *Flora*, 1892, 381).

Exclusive manuring with dung supplies to the soil a slight excess of readily available calcium over magnesium, and thus corrects to some extent any excess of magnesium in the soil. When mineral manures are employed, an application of calcium will be necessary, even when superphosphate is included in the manures.

In the case of most cereals, the best relation, $\text{CaO} : \text{MgO}$, is about 1. With other crops, especially the more leafy ones, twice or three times as much lime is required. N. H. J. M.

Composition of Beet Leaves and Heads Stored by the Rosam Process. O. FALLADA (*Bied. Centr.*, 1903, 32, 834—836; from *Oesterr.-Ung. Zeit. Zuckerind. Landw.*, 32, Heft. 1).—The leaves are heaped in the field and covered with soil. The composition of a sample of the fodder was found to be as follows :

| Water. | Proteids. | Non-proteid nitrogen. | Ether extract. | Pentoses. | N-free extract. | Crude fibre. | Sand. |
|--------|-----------|-----------------------|----------------|-----------|-----------------|--------------|-------|
| 78.09 | 1.28 | 0.81 | 0.53 | 2.81 | 2.13 | 1.86 | 9.01 |

The digestibility of the crude proteid (65 per cent.) is about the same as in the fresh leaves (66 per cent.). The acid consisted mainly of lactic acid, no large amount of oxalic acid being present.

N. H. J. M.

Chemical Characters of Wines from Vines Attacked by Mildew. ÉMILE MANCEAU (*Compt. rend.*, 1903, 137, 998—1000).—The chief characteristic of wine derived from mildewed vines (the leaves were attacked, not the grapes) was an abnormally high percentage of proteids. The amount of nitrogen as ammonia was also high, and the wine contained less alcohol and more acid than the wine from vines treated with copper salts. N. H. J. M.

Manurial Value of Various Nitrogenous Manures, especially Green Manure and Farmyard Manure. ALEXIUS VON 'SIGMOND (*Landw. Versuchs-Stat.*, 1903, 59, 179—215).—Summer barley, followed by mustard and buckwheat the same year, and by summer rape the second year, was grown in a calcareous sandy soil (92 pots), without nitrogen and with various nitrogenous manures. Two other series of experiments (each with 92 pots), similar to the first but with some modifications, are also described.

The relative action (average of series 1 and 2) of the nitrogen of the various manures as compared with nitrogen in the form of nitrate

=100 was as follows: nitrogen as ammonia, 90; as horn-meal, 90; blood-meal, 67; cow urine, 62; dried pig dung, 57; young vetches in autumn, 78; lucerne hay in autumn and in spring, 59 and 62; rotted dung in autumn, 49; fresh dung in spring and in autumn, 41 and 50.

The relative value of dung is very similar to that indicated by Pfeiffer's pot experiments. N. H. J. M.

Action of Phosphoric Acid in Conjunction with Lime. HERMANN BACHMANN (*Bied. Centr.*, 1903, 32, 801—803; from *Fühling's Landw. Zeit.*, 1903, 52, 12).—Lime and basic slag together increased the yield of rye-grain; in the case of other phosphates, with the exception of superphosphate, the simultaneous application of lime caused no diminution in yield. The yield of oats (grain) was hardly increased at all when lime was applied with basic slag, and there was a loss of yield when lime was applied with superphosphate.

In the case of beet, the application of lime along with phosphoric acid increased the yield, except with bone-meal, when there was a slight decrease. No essential differences were observed in the leaves. The amount of lime was 1000 kilos. per hectare. N. H. J. M.

Value of "Forty per cent. Potassium Salts" as Compared with Kainite. WILHELM SCHNEIDEWIND (*Bied. Centr.*, 1903, 32, 803—805; from *Arb. deut. landw. Ges.*, 1903, *Heft.* 81. Compare *Abstr.*, 1902, ii, 581).—The results of experiments with mangels were irregular; kainite may be employed unless injurious to the mechanical properties of the soil. The experiments on meadow-land were indefinite. N. H. J. M.

Analytical Chemistry.

Preparation of Hydrogen Sulphide Water for use in Analysis. KARL SANDER (*Zeit. angew. Chem.*, 1903, 16, 1202).—A saturated solution of hydrogen sulphide may be conveniently prepared by having in readiness a solution of sodium sulphide (such as is used in zinc testing) and acidifying just before use with hydrochloric acid, with methyl-orange as indicator. It must, of course, be remembered that it contains sodium chloride. L. DE K.

Estimation of Chlorides, Bromides, and Iodides. STANLEY BENEDICT and JOHN F. SNELL (*J. Amer. Chem. Soc.*, 1903, 25, 1138—1141).—The method previously described (*Abstr.*, 1903, ii, 750) has been made a quantitative one. After estimating the total halogens as usual, the iodine and chlorine are estimated as follows, the bromine being found by difference.

Fifty c.c. of the solution are mixed with a sufficiency of potassium iodate and 5 c.c. of 50 per cent. acetic acid. This liberates the iodine,

which is then removed by agitation with carbon disulphide and finally titrated with sodium thiosulphate. After expelling the bromine by adding 5 c.c. of nitric acid of sp. gr. 1.18 and boiling, the excess of potassium iodate is removed by adding potassium iodide slightly in excess of the amount necessary to react with it and repeating the boiling, if necessary, with a further addition of 2 c.c. of nitric acid. When the liquid is colourless, it is neutralised with calcium carbonate and the chlorine is estimated volumetrically, as usual. L. DE K.

Rapid Estimation of Chlorine, Bromine, and Iodine in Organic Compounds by means of Sodium Peroxide. HANS H. PRINGSHEIM (*Ber.*, 1903, **36**, 4244—4246).—The substance is mixed with 16 to 18 times its weight of sodium peroxide, ignited in a covered iron crucible by passing a hot wire through a hole in the cover, the product dissolved in water, acidified with nitric acid, and precipitated with silver nitrate. T. M. L.

Reduction of Alkali Bromates with Hydrazine Sulphate and Hydroxylamine Sulphate. MAX SCHLÖTTER (*Zeit. anorg. Chem.*, 1903, **37**, 164—171).—A series of experiments showing that bromates may be quantitatively reduced to bromides by the action of hydrazine or hydroxylamine sulphate. When the latter is used, the liquid should be strongly heated, and the reaction is slower than in the case of the former. The author recommends either of these substances instead of zinc dust or formaldehyde for the reduction of bromates. L. DE K.

Gas-volumetric Estimation of Bromates. MAX SCHLÖTTER (*Zeit. anorg. Chem.*, 1903, **37**, 172—176).—The reduction of alkali bromates by means of hydrazine sulphate (see preceding abstract) takes place according to the equation $2\text{NaBrO}_3 + 3\text{NH}_2\cdot\text{NH}_2 = 2\text{NaBr} + 3\text{H}_2\text{O} + 6\text{N}$. A series of experiments have shown that the volume of nitrogen evolved may serve as a measure for calculating the amount of the bromate. Hydroxylamine sulphate is less suitable, as the reaction is somewhat more complicated. L. DE K.

Reactions of Barium Peroxide with Titanosulphuric Acid. Detection of Peroxides. C. REICHARD (*Chem. Zeit.*, 1904, **28**, 16—18).—Titanosulphuric acid is reputed to be an excellent test for hydrogen peroxide, with which it produces a very permanent yellow or orange-yellow colour. The author tried its effect on barium peroxide and, as was fully expected, the same reaction was obtained. The peroxides of sodium, potassium, and calcium also gave the reaction. Efforts, however, to obtain the reaction with the insoluble peroxides or higher oxides, such as lead peroxide, manganese peroxide, cobaltic oxide, nickel trioxide, resulted in failure.

The colour produced by the barium compound is not destroyed by hydrochloric, nitric, tartaric, or oxalic acids. Alkalis destroy the colour, but this reappears on adding acid; the solution is, therefore, a good indicator. Potassium cyanide added to the acid solution gradually weakens the colour. Potassium ferrocyanide gradually

turns the mixture green with production of a green precipitate. Potassium ferricyanide turns it dark brown without causing a precipitate. Zinc and sulphuric acid slowly decolorises the liquid, which then gradually turns blue. Potassium iodate has no effect.

L. DE K.

Estimation of Sulphur in Pyrites. R. SILBERBERGER (*Ber.*, 1903, 36, 4259—4260).—Polemical. A reply to Lunge (this vol., ii, 82).
T. M. L.

Estimation of Tellurium by Electrolysis. I. GIOVANNI PELLINI (*Atti R. Accad. Lincei*, 1903, [v], 12, ii, 312—315).—For the electrolytic estimation of tellurium, the author obtains the best results as follows: a weighed amount (0.1—0.2 gram) of pure tellurium dioxide, dissolved in 5 c.c. of concentrated hydrochloric acid, is mixed with 100—120 c.c. of a cold saturated solution of ammonium hydrogen tartrate and the liquid poured into a Classen's capsule with a matt surface, water being added to bring the total volume up to 160—170 c.c. The anode employed is a spiral of platinum wire, and the current used 0.02 ampere per 100 sq. cm. at first, and 0.014 ampere later, the voltage being 1.85—2.2; electrolysis is carried out at 55—65°, the volume of the liquid being kept constant by the addition of water. It is important not to carry on the electrolysis longer than is necessary, and to determine its completion, which requires 7—9 hours, about 2 c.c. of the solution are heated with a few drops of hydrochloric acid and stannous chloride; only a faint brown coloration should thus be produced, the reaction being as follows: $\text{H}_2\text{TeO}_3 + 2\text{SnCl}_2 + 4\text{HCl} = \text{Te} + 2\text{SnCl}_4 + 3\text{H}_2\text{O}$. Without interrupting the current, the deposited tellurium is washed, as far as possible out of contact with air; water which has been boiled and allowed to cool in a current of carbon dioxide is best used. The current is then stopped, the liquid carefully decanted off, and the precipitate washed once with dilute alcohol and several times with absolute alcohol, then dried for 15 minutes at 100° and weighed. The results obtained in this way were very good, and confirm the value 127.6 for the atomic weight of tellurium.

T. H. P.

Modification of the Pelouze-Fresenius Method of Estimating Nitric Acid. LÉON DEBOURDEAUX (*Bull. Soc. chim.*, 1904, [iii], 31, 1—3).—The apparatus used is the same as that devised by Fresenius. The sample of the nitrate is placed in a flask through which a stream of carbon dioxide is passed to displace the air. After one hundred c.c. of a ferrous iron solution (150 grams $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 500 c.c. of sulphuric acid, and water to 2 litres) have been added, the mixture is slowly heated until decolorised. When the solution is cold, the remaining ferrous iron can be titrated in the usual way with permanganate, and the nitrate in the original sample calculated.
S. S.

The Unsuitability of the Maercker-Bühring Solution for the Estimation of Total Phosphoric Acid in Basic Slags. H. SVOBODA (*Chem. Zeit.*, 1903, 27, 1203—1205).—The so-called

Maercker-Bühning solution consists of a solution of 1500 grams of citric acid, and 5 litres of ammonia of sp. gr. 0.91, made up with water to 15 litres, and is used in the analysis of basic slags. The author states that this solution rapidly dissolves silica from the glass, which afterwards contaminates the magnesium pyrophosphate and so gives erroneous results.

L. DE K.

Estimation of Citrate-soluble Phosphoric Acid in Basic Slags. OSKAR BÖTTCHER (*Chem. Zeit.*, 1903, 27, 1225).—One hundred c.c. of the citric acid solution of the basic slag are boiled in a 200 c.c. flask with 75 c.c. of ammoniacal citrate solution, and if after remaining for 10 minutes no precipitate is perceptible, the liquid is free from silica, and another 50 c.c. of the solution are treated as usual for phosphoric acid. Should, however, a precipitate form, the liquid is slightly acidified with hydrochloric acid and diluted to the mark. After filtering, 100 c.c. of this liquid, now free from silica, are taken for analysis.

L. DE K.

Arsenious Iodide. WILLIAM DUNCAN (*Pharm. J.*, 1904, [iv], 18, 8).—The purity of samples of arsenious iodide can be readily determined by dissolving a weighed quantity of the salt in solution of sodium or potassium bicarbonate and titrating with iodine.

The anhydrous salt, prepared by crystallisation from hot carbon disulphide, is fairly stable provided that moisture is excluded. E. G.

Estimation of Rubidium and Cæsium. CLEMENTE MONTE-MARTINI and G. MATTUCCI (*Gazzetta*, 1903, 33, ii, 189—201).—Gilbert's method of estimating potassium (*Diss. Tübingen*, 1898) by conversion into potassium perchlorate is applied to the estimation of rubidium and cæsium. The rubidium or cæsium is first precipitated by an excess of sodium cobalt nitrite solution, prepared according to Gilbert's method, the temperature being maintained at 40° for six or seven hours; after leaving overnight, the precipitate is collected, washed first with the reagent, subsequently with alcohol, and decomposed at 300°. The residue is extracted with boiling water and the solution evaporated to dryness several times with hydrochloric acid to convert the metal into chloride; the product is then redissolved, several c.c. of a 30 per cent. solution of perchloric acid added, and the solution evaporated to remove excess of perchloric acid. After extraction with absolute alcohol, the insoluble perchlorate is dried at 110° and weighed.

A series of analyses are given showing that this method gives good results in the presence of lithium, magnesium, calcium, barium, aluminium, iron, nickel, cobalt, and copper salts; the metals may be combined as chlorides, acetates, nitrates, and sulphates.

The composition of the precipitates obtained with sodium cobalt nitrite in the case of rubidium or cæsium is not definite, sodium always being present to the extent of 4—5 per cent. Gilbert has stated that when the corresponding potassium cobalt nitrite is precipitated in presence of such metals as iron, calcium, and magnesium, these elements are not co-precipitated; it is shown, however, that the precipitates contain considerable quantities of these metals, although

this fact does not interfere with the accuracy of the final conversion into perchlorate, products being ultimately formed which are easily soluble in alcohol.

W. A. D.

Reducing Action of Aluminium in Quantitative Analysis. NAZARENO TARUGI (*Gazzetta*, 1903, ii, 223—233. Compare Abstr., 1902, ii, 141).—Silver can be estimated by acidifying a solution of the nitrate with sulphuric acid and adding a thin strip of aluminium to the solution; after 2 or 3 hours the silver is deposited as metal quantitatively in the form of small, lustrous crystals. On the other hand, the precipitation of copper from its sulphate in presence of sulphuric or hydrochloric acid, or from copper sulphate to which sodium potassium tartrate or potassium hydroxide has been added, is very incomplete; this is due to the formation of cuprous sulphite, which in certain dilutions is not reduced by aluminium. In presence of alkali salts, for instance, potassium sulphate, the ratio of copper found to copper used is nearly constant, namely, about 1.5, a fact which would point to the formation of a double sulphite according to the equation: $6\text{CuSO}_4 + 2\text{K}_2\text{SO}_4 + 7\text{H}_2 = \text{Cu}_2\text{SO}_3 \cdot \text{K}_2\text{SO}_3 + 4\text{Cu} + 2\text{KHSO}_4 + 4\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$.

W. A. D.

Separation of Barium, Strontium, and Calcium. LUCIEN ROBIN (*Ann. Chim. anal.*, 1903, 8, 445—447).—The nitric or hydrochloric acid solution of the three earths is neutralised with ammonia, 2 per cent. of ammonium chloride is added, and after acidifying with a little acetic acid the barium is precipitated at the boiling heat with an excess of solution of potassium dichromate. The precipitated barium chromate is first washed with a warm 2 per cent. solution of ammonium acetate, then with dilute alcohol (1:9), dried at 110°, and weighed. The filtrate is mixed with slight excess of ammonia, heated to boiling, and the strontium is precipitated as sulphate by adding 3 per cent. of ammonium sulphate and boiling for 15 minutes. The precipitate is washed with a one-half per cent. solution of ammonium sulphate, then with dilute alcohol, and finally ignited and weighed.

The calcium is then precipitated as usual by means of ammonium oxalate.

L. DE K.

[Separation of Indium and Zinc.] Correction. CARL RENZ (*Ber.*, 1903, 36, 4394. Compare Abstr., 1901, ii, 657).—Indium and zinc cannot be separated by the method previously described.

J. J. S.

Rivot's Estimation of Iron in the presence of Zirconium. KARL DANIEL (*Zeit. anorg. Chem.*, 1903, 37, 475—476. Compare Abstr., 1902, ii, 701; 1903, ii, 392).—A reply to Gutbier (this vol., ii, 90).

L. DE K.

A Delicate Reaction of Titanium. ARMAND JORISSEN (*Bull. Acad. Roy. Belg.*, 1903, 902—907).—The author makes use of the fact that titanium sulphate gives a red coloration with salicylic acid to detect small quantities of titanium in minerals. The material is

fused in a bead of acid-potassium sulphate and introduced into a solution of 0.01—0.02 gram of salicylic acid in 20—30 drops of concentrated sulphuric acid; the production of a red colour indicates the presence of titanium. The reaction may be used with substances containing cerium, aluminium, glucinum, lanthanum, didymium, thorium, zirconium, chromium, and silicon. In presence of vanadium, molybdenum, and tungsten, the test is not applicable. S. S.

Separation of Antimony and Tin with Oxalic Acid. F. HENZ (*Zeit. anorg. Chem.*, 1903, 37, 1—58).—A lengthy investigation as to the best forms for weighing tin and antimony and their separation.

The results may be summarised as follows: *Antimony*.—The estimation as trisulphide is the most accurate, but good results are also obtained by weighing it as tetroxide according to Bunsen's original directions. If it is desired to separate the metal by electrolysis, this should be effected by using an alkaline sulphide solution mixed with sodium sulphite or potassium cyanide.

Tin.—The best method for estimating this element is the electrolytic separation from an oxalic acid solution according to Classen's method; the separation from an ammonium sulphide solution is not to be recommended, as the metal separates in a spongy condition. *Separation*.—The Clarke-Rössing method does not give a complete separation, but a good separation is effected by oxidising the alkaline solution of the sulpho-salts in the presence of potassium tartrate with hydrogen peroxide, then adding excess of oxalic acid, and precipitating the antimony with hydrogen sulphide at the boiling heat. L. DE K.

Herroun and Weller's Process for the Volumetric Estimation of Antimony. LEWIS A. YOUTZ (*Zeit. anorg. Chem.*, 1903, 37, 337—352).—The author has critically studied the volumetric process proposed by Herroun and by Weller (*Abstr.*, 1882, 661, 1324) and found it to be well suited for technical purposes, 99 per cent. of the antimony present being recovered. In order, however, to get trustworthy results, the following conditions should be adhered to.

The antimony sulphide, obtained from an ore in the usual manner and representing 0.2—0.25 gram of metal, is dissolved in hydrochloric acid with addition of 1 c.c. of nitric acid, and the oxidation is completed by addition of small portions of potassium chlorate. The solution is concentrated to 50 c.c. Fifteen to twenty c.c. of strong hydrochloric acid are added, and the whole is diluted to 700 c.c. After adding 3—4 grams of potassium iodide to the cold solution, the liberated iodine, which represents the antimony, is without delay titrated with standard solution of sodium thiosulphate. L. DE K.

Titration of Minute Quantities [especially of Gold]. ERWIN RUPP (*Ber.*, 1903, 36, 3961—3965).—A reply to Maxson's criticism (*Abstr.*, 1903, ii, 697) of the author's method for estimating small quantities of gold (*Abstr.*, 1902, ii, 479). It is contended that Maxson's own experimental data refute his arguments, and that Gooch and Morley's method is not so accurate as that of the author. A

general discussion of the errors likely to arise in estimating small quantities is based on the data arising from this special question.

W. A. D.

Separation of Gold, Silver, and Platinum. H. CARMICHAEL (*J. Soc. Chem. Ind.*, 1903, 22, 1324—1325).—The results of a series of experiments are given, from which it is seen that 7 per cent. of platinum in gold is the highest ratio that can be successfully parted. The process consisted in wrapping the alloy in sheet lead, cupelling, parting firstly in nitric acid of sp. gr. 1.162, and afterwards in nitric acid of sp. gr. 1.284. The resulting gold cornet was free from platinum. The alloy employed was composed of 0.100 gram of gold, 0.007 gram of platinum, and 0.500 gram of silver. Mass seemed to play a part in this separation, as when double these weights were taken the cornet did not part, but on increasing the proportion of gold, it parted satisfactorily.

The separation of silver in alloys of gold, silver, and platinum is best carried out by cupelling, parting the cornet with dilute sulphuric acid, washing, and then treating with concentrated nitric acid.

The wet method for the estimation of platinum in alloys was found to be untrustworthy.

In the case of ores or black sands, the separation of the osmium-iridium group from the noble metals presents no difficulty if a little silver is present. The lead button, obtained by fusing the ore in the usual manner, is boiled with dilute sulphuric acid (1:10), gradually allowing the acid to become more concentrated. After washing, the button is boiled with nitric acid, again washed, and finally dissolved in *aqua regia*, when the osmium-iridium group alone remains insoluble, with perhaps a trace of silver chloride, which may be removed by treatment with ammonia.

W. P. S.

Estimation of Hardness in Waters. FRIEDRICH AUERBACH (*Chem. Zeit.*, 1904, 28, 16).—The author does not agree with Drawe (*ibid.*, 1903, 27, 1219) that the slight alkalinity of water after boiling is necessarily due to alkali carbonate, but ascribes it to the presence of magnesium carbonate, which is more soluble than is generally supposed.

L. DE K.

Estimation of Hardness in Water. E. BASCH (*Chem. Zeit.*, 1904, 28, 31).—The author is inclined to agree with Drawe (see preceding abstract) that the permanent alkalinity in natural waters is due to alkali carbonate.

L. DE K.

Volumetric Estimation of *p*-Nitrotoluene in Crude Nitrotoluene. B. GLASMANN (*Ber.*, 1903, 36, 4260—4261).—The nitrotoluene is reduced with iron and hydrochloric acid, and a weighed quantity of the resulting toluidine is dissolved in ether and the *p*-toluidine precipitated with ethereal oxalic acid and well washed with ether; the oxalate is dissolved in water and titrated with decinormal sodium hydroxide, using phenolphthalein as an indicator.

T. M. L.

Estimation of Citric Acid by the Lime Method. O. VON SPINDLER (*Chem. Zeit.*, 1903, 27, 1263—1264).—The author has proved by a series of experiments that calcium citrate is but very incompletely precipitated on boiling its solution containing ammonium chloride and ammonia, and that the calcium process for the gravimetric estimation of citric acid is, therefore, quite untrustworthy.

L. DE K.

Detection of Tartaric Acid in Citric Acid. O. VON SPINDLER (*Chem. Zeit.*, 1904, 28, 15—16).—A modification of Denigès's process, potassium dichromate being substituted for potassium permanganate.

0.5 gram of the acid to be tested is dissolved in 10 c.c. of water, 2 c.c. of Denigès's mercury solution (5 grams of mercuric oxide, 20 c.c. of sulphuric acid, 80 c.c. of water) are added, and after being heated to boiling, 2 c.c. of dichromate solution (5:1000) are introduced. When the citric acid is pure, a bright yellow precipitate forms, and the liquid remains clear yellow for several days, but in the presence of tartaric acid reduction takes place as seen by the change in colour. The method cannot be employed for the determination of citric acid, as the composition of the precipitate is not constant.

L. DE K.

Use of Amyl Alcohol in the Estimation of Fat in Milk by Gerber's Method. MORITZ SIEGFELD (*Zeit. angew. Chem.*, 1903, 16, 1217—1220).—A series of experiments on the composition of various samples of amyl alcohol and their action with sulphuric acid of varying concentration.

The author finally arrives at the same conclusion as van Haarst (*Abstr.*, 1903, ii, 516), that it is not safe to use a fresh supply of amyl alcohol for Gerber's process unless it has been practically tested. A yellow colour is not necessarily a bad sign.

L. DE K.

Detection of Albumin in Urine. ÉMILE DUFAU (*J. Pharm. Chim.*, 1903, 18, [vi], 389—392).—The urine, which must be acid in reaction, is heated as usual in a test-tube with 0.1 c.c. of a solution of 250 grams of sodium citrate and 50 grams of alcohol in 1000 c.c. of water. Phosphates are not precipitated by this solution, but albumin is, if present.

W. P. S.

Forensic Detection of Blood. FRANZ UTZ (*Chem. Zeit.*, 1903, 27, 1151—1152).—Meyer's process is recommended. The suspected spot is treated with an alkaline solution of phenolphthalin (obtained by reducing an alkaline solution of phenolphthalein with zinc dust) and a few drops of a 0.1 per cent. solution of hydrogen peroxide are added. If blood is present, reoxidation takes place and the colour turns pink.

L. DE K.

General and Physical Chemistry.

Line Spectra of the Alkalies. HEINRICH KONEN and AUGUST HAGENBACH (*Chem. Centr.*, 1903, ii, 1361; from *Physikal. Zeit.*, 4, 801).—The arc spectrum of sodium shows a number of lines which can be arranged in special series, and, on account of their number and position, suggest a comparison with the spectra of the helium group. Similar series exist in the case of lithium, but not in that of any other alkali metal, so far, at least, as the present investigation has shown. The wave-lengths of the new lines observed in the arc spectrum of lithium are 6240·8, 4636·14, 4149·1, 3924; the lines, however, are not sharply defined. A number of rubidium lines, hitherto unnoticed altogether, or not detected in the arc spectrum, have been measured and shown to belong to already known series.

J. C. P.

A New Burner for Spectra. Apparatus for collecting Gases for Lecture Experiment Purposes. ERWIN RUPP (*Zeit. anorg. Chem.*, 1904, 38, 107—109).—A description of a combined atomiser and burner for spectroscopic purposes or for furnishing monochromatic light, and also of a convenient arrangement of a glass trough and cylinders for collecting gases on the lecture table. A. McK.

Determination of Specific Rotation by Kanonnikoff's Method. ALEXEI A. PANORMOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 678—687).—The author has made a number of measurements of the rotatory power of French turpentine, *l*-pinene, cholesterol, and quinine hydrochloride in chloroform solutions. The results show that Kanonnikoff's method (Abstr., 1889, 326) of deriving the specific rotation of a compound from polariscopic readings of two solutions of different concentration, and also the author's modification of this method (*J. Russ. Phys. Chem. Soc.*, 1894, 26, 193), can only be applied in special cases and not generally, since the constant *A* employed varies with the concentration, and α depends not only on the solvent, but also on the substance dissolved.

T. H. P.

Specific Rotations of some Proteids and their Derivatives. ALEXEI A. PANORMOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 688—690).—As the method used by the author in determining the specific rotations of proteids is an incorrect one (see preceding abstract), he has made new measurements to replace his previous determinations (Abstr., 1899, i, 654 and 655; Maximowitsch, Abstr., 1902, i, 66). The new values are higher than the older ones, but the changes do not affect the conclusions previously deduced.

T. H. P.

Influence of Temperature on the Specific Rotatory Power of Strongly Optically Active Compounds. HERMANN GROSSMANN and HEINZ PÖTTER (*Ber.*, 1904, 37, 84—88. Compare Itzig, Abstr., 1901, i, 448 and 580).—Ammonium molybdanyldimalate,

$$\text{MoO}_2(\text{C}_4\text{H}_5\text{O}_5\cdot\text{NH}_4)_2,$$

is remarkable in that its specific rotatory power increases with temperature until a maximum is reached at 35° , after which it diminishes continuously, but at a slower rate than during the increase, thus during the change of temperature from 10° to 35° , $[M]_D$ for the complex salt in a 19.343 per cent. solution increases from -122° to -129.5° , whilst a subsequent increase of temperature to 95° only causes a decrease to -118.9° . The diminution of rotatory power of the complex salt with increasing dilution at the ordinary temperature is small compared with that of the dimolybdanylmalates (Itzig, *loc. cit.*) under similar conditions, thus proving a relatively greater stability.

The behaviour of potassium and sodium molybdanyltartrates, $\text{MoO}_2(\text{C}_4\text{H}_5\text{O}_6\text{K})_2$, is normal, the specific rotatory power diminishing continuously with the temperature. But sodium molybdanyldimalate, like the ammonium salt shows a maximum rotatory power at a temperature of 50° .

W. A. D.

Radioactive Substances. SKŁODOWSKA CURIE (*Ann. Chim. Phys.*, 1903, [vii], 30, 145—203; 289—326).—The conclusion of the author's thesis (compare Abstr., 1903, ii, 622), comprising a full description of (1) the characteristic properties of the α -, β - and γ -rays of the radium radiation (compare Abstr., 1900, ii, 126, 254, 381); (2) their physical, chemical, and physiological effects (compare Abstr., 1900, ii, 125, 330; 1901, ii, 99; 1903, ii, 346, 462); (3) the phenomenon of induced radioactivity (compare Abstr., 1900, ii, 586; 1901, ii, 19, 215, 216, 298, 385, 589; 1902, ii, 58, 190; 1903, ii, 50, 255); (4) the atomic weight of radium (compare Abstr., 1900, ii, 83, 654; 1902, ii, 562).

M. A. W.

Analogy between Radioactivity and the Behaviour of Ozone. FRANZ RICHARZ and RUDOLF SCHENCK (*Sitzungsber. K. Akad. Wiss. Berlin*, 1903, 1102—1106).—Freshly prepared ozone, or ozone that is decomposing under the influence of desozoneising agents, accelerates the condensation of water vapour. The presence of gaseous ions, to which this phenomenon points, is confirmed by the considerable conductivity exhibited by ozone. In respect of this ability to produce gaseous ions, ozone is similar to radium and other radioactive substances. Further, a current of ozonised oxygen causes a zinc sulphide screen to fluoresce, although barium platinocyanide and zinc oxide are unaffected. Another point of analogy is the fact that radium salts and ozone both decompose with considerable development of heat.

J. C. P.

Voltaic Elements founded on the Reciprocal Action of Saline Liquids and of Metallic Electrodes. Preliminary Observations on the Methods of Measurement and Conditions of Experiment. MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1903 [vii], 30, 433—435, 435—451. Compare Abstr., 1903, ii, 51, 125).—These papers are introductory to nine others, the titles of which are appended, and contain a detailed description of the method employed and the apparatus used, in connection with which it may be stated that the electromotive force was measured by means of Arsonval's

galvanometer or of Lippmann's capillary electrometer, and in working with elements involving the use of more than two liquids, a gutta percha vessel was used, divided into the necessary number of compartments by means of septa of parchment paper, cemented in position with gutta percha.

A Law relating to the Electromotive Force of Voltaic Elements Based on the Reciprocal Action of Salt Solutions and Soluble Electrolytes, and Particularly with the Reaction of an Acid and a Base (*ibid.*, 451—469. Compare Abstr., 1903, ii, 258). Law of Electromotive Forces of Salt Solutions : (1) Influence of Temperature and of Concentration (*ibid.*, 469—475. Compare Abstr., 1903, ii, 259). (2) Influence of the Nature of the Electrodes (*ibid.*, 475—487. Compare Abstr., 1903, ii, 464). Generalisation of the Law relating to the Electromotive Forces of Saline Solutions (*ibid.*, 487—506. Compare Abstr., 1903, ii, 524, 526). Researches on Voltaic Elements of One and of Two Liquids ; Theoretical Relations and Verifications (*ibid.*, 506—515. Compare Abstr., 1903, ii, 525). Relations between Voltaic Elements of Several Liquids with identical or different Electrodes (*ibid.*, 515—521. Compare Abstr., 1903, ii, 625). Remarks concerning the Relationships between Galvanic Elements containing the same Liquids between two different or identical Electrodes (*ibid.*, 521—528. Compare Abstr., 1903, ii, 626). New Researches on Galvanic Elements with Several Different Liquids and Identical Metallic Electrodes (*ibid.*, 528—542. Compare Abstr., 1903, ii, 626). General Observations on Galvanic Elements with Two Liquids, Electromotive Forces, Condensations, Transformation of Energy at the Electrodes (*ibid.*, 542—554. Compare Abstr., 1903, i, 524 ; this vol., ii, 9). M. A. W.

Iron Salts in Voltameter Solutions. JAMES M. BELL (*J. Physical Chem.*, 1903, 7, 652—655).—The presence of iron in the sulphuric acid solution in a hydrogen voltameter lowers materially the volume of gas evolved, but in the solution in a copper voltameter the presence of iron has but a negligible effect. These results are not contradictory, as there is an essential difference between the two cases owing to the hydrogen voltameter possessing an insoluble anode, and the author's experiments show that with a platinum anode there is also a decrease of copper deposited per ampere. The author considers the cause to be the oxidation of ferrous to ferric salt at the anode with the corresponding reduction at the cathode. L. M. J.

Action of Radium Bromide on the Electric Resistance of Bismuth. R. PAILLOT (*Compt. rend.*, 1904, 138, 139—140).—The resistance of a spiral of bismuth wire is considerably diminished when the latter is placed in the neighbourhood of radium bromide. A wire of resistance 15.1034×10^{-4} ohms was placed 0.5 mm. distant from 0.03 gram of radium bromide (activity = 500,000) ; in these circumstances, the resistance of the bismuth spiral was reduced by 52×10^{-4} ohms. The action of the radium salt is instantaneous, and remains constant as long as the distance from the wire is unaltered.

S. S.

Electrical Conductivity of Solutions in Bromine. WLADIMIR A. PLOTNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 794—810. Compare Abstr., 1902, ii, 639).—Bromine solutions of pure aluminium bromide and also of mixtures of aluminium bromide with iodine do not conduct a current, but solutions of about 10 per cent. or higher concentration of the complex compounds, AlBr_7CS_2 and $\text{AlBr}_5\text{EtBrCS}_2$, in bromine exhibit a conductivity which is moderately high and much greater than for more dilute solutions; thus, for solutions of various concentrations of the former compound, the values of K are as follows: 9.9 per cent., $34 \cdot 10^{-8}$; 10.3 per cent., 0.0027; 11.5 per cent., 0.0037; 14.2 per cent., 0.0053, and 29.2 per cent., 0.0057. Bromine solutions of antimony tribromide or phosphorus pentabromide also conduct.

It is possible that other "non-ionising" solvents also yield solutions capable of conducting, and this property may depend on the "conformity" between the solvent and the dissolved substance.

T. H. P.

Relation between the Conductivity of Selenium and the Intensity of the Incident Light. E. A. HOPIUS (*J. Russ. Phys. Chem. Soc.*, 1903, 35, ii, 581—583).—The author has made a number of experiments on the conductivity of selenium illuminated by means of a normal amyl acetate lamp or a Nernst lamp placed at different distances. The intensities of the currents produced were measured by special apparatus, and the values obtained show that the increase of the conductivity of selenium is approximately proportional to the cube root of the intensity of illumination.

T. H. P.

Influence of Temperature on the Electrical Conductivity of Sodium. ARCIERO BERNINI (*Nuovo Cim.*, 1903, [v], 6, 21—30).—Measurements of the specific resistance of sodium in the solid and liquid states are given at temperatures from 0—130°, which shows that the metal is one of the best of metallic conductors, and that its resistance increases proportionately to the increase of temperature. The temperature coefficient is extraordinarily high; thus the resistance of the solid at 90° is 1.38484 times that at 0°, the corresponding values for mercury being 1.08615:1. At 0°, the conductivity is 19.84 referred to the mercury unit, at 120° (liquid), it is 10.74. The value of the ratio of the resistances in the liquid and solid state at the melting point is 1.342, referred to mercury.

W. A. D.

Electrical Conductivity of Solutions of Vanadyl Trichloride in Water. A. A. AGAFONOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 649—651).—The author has measured from time to time the electrical conductivities of aqueous solutions of vanadyl trichloride, which, as is known, become turbid and intensely lemon-yellow when kept for a long time in sealed vessels. He finds that the value of the conductivity undergoes a corresponding change. Thus, at 18°, a freshly prepared solution containing 1 gram-mol. of vanadyl trichloride in 74.06 litres of water has a conductivity of 179.77, which increases to 200.83 after 46 days, and diminishes to 178.34 after a further 9 days. On heating a solution 42 days old to 30°, 60°, 70°, and 80°, and cooling

again to 18° , the values obtained for the conductivity were 192.95, 214.98, 218.97, and 216.96 (or, when slowly cooled, 202.93) respectively.
T. H. P.

Change in the Specific Conductivity of Solutions of Salts produced by Alkali Hydroxides. RICHARD EHRENFELD (*Zeit. Elektrochem.*, 1904, 10, 3—9).—Successive drops of a very dilute solution of an alkali hydroxide are added to solutions of salts, and the conductivity measured after each addition (Abstr., 1903, ii, 548). A small diminution of conductivity is produced by the first two or three drops, the succeeding drops producing an increase. This was found to be the case with the potassium salts of tartronic, tartaric, malic, tri-carballylic, citric, and aconitic acids, and the sodium salts of fumaric, maleic, benzenesulphonic, picric, and lævulic acids. The phenomenon was, however, also observed in the case of salts which are known to be hydrolysed in aqueous solution, such as borax, potassium or sodium acetate, carbonate, sulphite, nitrite, and chromate, and ammonium chloride, sulphate, and nitrate. Even the salts of strong acids with strong bases, such as sodium and potassium nitrates and sulphates and sodium chloride, show it somewhat; potassium chloride was the only salt with which it could not be observed. These results lead to the view that the diminution of conductivity is due to diminution of the hydrolytic dissociation of the salts and not to the acid nature of a methylene group, as the author previously supposed (Abstr., 1903, ii, 548).
T. E.

Electrical Conductivity of Solutions of Oxalic Acid in presence of Neutral Salts. A. FEDOROFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 651—652).—Electrical conductivity measurements, by the Kohlrausch-Ostwald method, of a solution of oxalic acid containing either ammonium chloride or oxalate, show that the former of these salts diminishes the conductivity, whilst the latter increases it.

T. H. P.

Physico-chemical Properties of Aqueous Solutions of Salts of Lanthanum, Cerium, and Thorium. KNUT HOLMBERG (*Arkiv Kem. Min. Geol.*, 1903, 1, 1—32).—The author has measured the decomposition tensions of lanthanum, cerium, and thorium chlorides in normal solutions, the results being as follows: LaCl_3 , 1.86 volts; CeCl_3 , 1.12 volts, and ThCl_4 , 1.69 volts. Since $S_{\text{Cl}} = -1.31$ volts, the values of S for La, Ce (ceric), and Th are 0.55, -0.19 , and 0.38 volt respectively.

Electrolytic conductivity measurements were also made at 0° and 18° of solutions of $\text{La}_2(\text{SO}_4)_3$, $\text{Ce}_2(\text{SO}_4)_3$, $\text{Th}(\text{SO}_4)_2$, LaCl_3 , CeCl_3 , and ThCl_4 . The conductivities at infinite dilution are calculated to be as follows: for $\text{La}_2(\text{SO}_4)_3$ at 18° , 116, and at 0° , 76; for $\text{Ce}_2(\text{SO}_4)_3$ at 18° , 122, and at 0° , 80; for LaCl_3 at 18° , 112, and at 0° , 69; for CeCl_3 at 18° , 118, and at 0° , 72.

For measuring the hydrolytic dissociation of these salts, the author proposes to use a method based on the theory of the concentration element. Of two cylinders, the bases of which are connected by a narrow tube, one contains the salt solution to be examined, and the

other the corresponding acid in equivalent quantity; in each solution is placed a large hydrogen gas electrode. Since the solution tension of the hydrogen is the same for the two electrodes, the *E.M.F.* of such a concentration element is calculated from the expression:

$$E = RT \log. c_2/c_1 + \epsilon,$$

where c_2 and c_1 are the concentrations of the hydrogen ions in the salt solution and acid respectively, and ϵ the *E.M.F.* at the surface of separation of the two solutions; c_2 , which determines the hydrolytic dissociation of the salt solution, is the only unknown quantity in this equation.

T. H. P.

Laboratory Apparatus for Fractional Distillation. ALBERT VESTERBERG (*Arkiv Kem. Min. Geol.*, 1903, 1, i, 33—60).—The author has made experiments on the relative values of various types of fractional distillation apparatus, including Le Bel and Henninger's, Hempel's, a spiral condenser, a combination of the last-named with a tube containing beads, &c.

The construction of such an apparatus should be based on the following principles: (1) the path, which the vapour and condensed liquid have to traverse in opposite directions, should be as long as possible. (2) The condensed liquid should be spread over as large a surface as possible, and the contact between it and the vapour should be as intimate as possible. (3) In order that the velocity of the ascending stream of vapour may not be too great, the distillation should be carried on slowly, and the sectional area of the condenser should be tolerably great. (4) The partial condensation should not be too weak, nor so strong that the condenser becomes stopped (compare Young, *Trans.*, 1899, 75, 679; *Abstr.*, 1901, ii, 86).

T. H. P.

An Apparatus for the Determination of Molecular Weights by Elevation of the Boiling Point. JOHAN F. EIJKMAN (*Chem. Centr.*, 1903, ii, 1407—1408; from *Chem. Weekblad*, 1, 47—50).—The apparatus consists essentially of three concentric tubes, of which the outermost contains the solvent and the innermost the solution. The volume of the latter can be read from a special graduation made for the purpose on the thermometer. The molecular boiling point elevations (referred to 100 c.c. of solvent) have been determined for *cyclohexane* and *cyclopentane*, and found to be 37—38 and 27—27·8 respectively.

J. C. P.

Critical Temperatures of Solutions. I, II, and III. MIECZYSŁAW CENTNERSZWER (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 742—766, 766—793, and 897—935).—The author first gives an account of previous work done on the critical temperatures of solutions, and then describes in detail the methods of measurement of the critical temperature employed in his own investigations. The solvents made use of were ammonia, which has a critical point of $132\cdot53^\circ \pm 0\cdot2^\circ$ on the normal hydrogen thermometer, and sulphur dioxide, the critical temperature of which is $157\cdot26^\circ \pm 0\cdot2^\circ$ on the same scale. Solutions in these solvents of a number of organic compounds of various types (all non-electrolytes), hydro-

carbons, amines, alcohols, ketones, esters, and amides, were examined, and the results obtained are given in detail.

The value obtained for the critical temperature of a liquid is dependent on the following conditions. (1) *The Extent to which the Tube is Filled*.—The temperature at which the meniscus of a pure solvent disappears when the containing tube is gradually heated and kept continually in motion depends on the amount of liquid in the tube, and, whether this is small or large, is always lower than the true critical temperature, which is obtained when the disappearing meniscus is in the middle of the tube. With solutions, however, it is otherwise, for in this case the temperature at which the meniscus disappears in a tube containing a large volume of the solution is always lower, and with small volumes higher, than the true critical temperature. These facts are shown to be in accordance with the theory of the condensation of binary mixtures. (2) *Concentration*.—The extent to which the true critical temperature (meniscus in the middle of the tube when it disappears) of a solvent is raised by a dissolved substance is proportional to the concentration of the solution, so that if ϑ_0 represent the critical temperature of the pure solvent, and ϑ that of a solution containing n gram-mols. of dissolved substance per 100 grams of solvent, $\vartheta - \vartheta_0 = K n$, where K is a constant coefficient for a particular solvent. This expression is seen to be perfectly analogous with those connecting the depression of freezing point, rise of boiling point, &c., of a solution with its concentration. (3) *Nature of the Dissolved Substance*.—For one and the same solvent, the coefficient K has a nearly constant value for all dissolved substances, the boiling points of which under the ordinary pressure are more than 100° higher than the critical temperature of the solvent. Dissolved substances having boiling points nearer than this to the critical point of the solvent give values for K considerably less than the normal. (4) *Nature of the Solvent*.—The limited data do not allow of safe generalisation, but for ammonia and sulphur dioxide the molecular weight of the solvent divided by K gives the same number, and this is also found to be the case for chloroform.

T. H. P.

Determination of the Heats of Combustion of Alcohols of the Aliphatic Series and an Oxime. PAWEL ZUBOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 815—824. Compare Abstr., 1899, ii, 589, and 1902, i, 144).—The following heats of combustion have been determined by the author, using Regnault's value for the specific heat of water; the numbers represent calories per gram-molecule.

| | Constant volume. | Constant pressure. |
|---|---------------------|-----------------------|
| $C_6H_{14}O$, Pinacolin alcohol | 946·3 | 948·0 |
| Methyldiethylcarbinol..... | 934·6 | 936·3 |
| $C_7H_{16}O$, Triethylcarbinol | 1088·7 | 1090·7 |
| $C_8H_{18}O$, Methyldipropylcarbinol | 1242·7 | 1245·1 |
| $C_9H_{20}O$, Ethyldipropylcarbinol | 1397·6 | 1400·2 |
| $C_6H_{12}O$, Dimethylallylcarbinol | 894·1 | 895·5 |
| $C_7H_{14}O$, Methylethylallylcarbinol... .. | 1059·0 | 1060·7 |

| | Constant volume. | Constant pressure. |
|---|---------------------|-----------------------|
| C ₈ H ₁₆ O, Methylpropylallylcarbinol | 1212·0 | 1214·0 |
| Diethylallylcarbinol..... | 1217·2 | 1219·3 |
| C ₉ H ₁₈ O, Methyl- <i>n</i> -butylallylcarbinol..... | 1376·3 | 1378·7 |
| Methyl- <i>tert</i> .-butylallylcarbinol... | 1374·4 | 1376·8 |
| C ₁₀ H ₂₀ O, Dipropylallylcarbinol | 1530·5 | 1533·2 |
| C ₁₁ H ₂₂ O, Methylhexylallylcarbinol | 1680·3 | 1683·2 |
| C ₇ H ₁₂ O, Dialllylcarbinol..... | 1037·3 | 1038·7 |
| C ₈ H ₁₄ O, Methylallylcarbinol | 1191·0 | 1192·7 |
| C ₁₀ H ₁₈ O, Propyldiallylcarbinol | 1484·7 | 1487·0 |
| C ₇ H ₁₄ O, 1 : 3-Dimethylcyclopentanol-3... | — | 1044·4 |
| C ₈ H ₁₆ O, 1 : 3-Dimethylcyclohexanol-3 ... | — | 1204·5 |
| Methylcycloheptanol | — | 1201·4 |
| Methylethylketoxime | 652·3 | 653·0 |

On comparing these values with those previously obtained (*loc. cit.*) for aromatic compounds, it is found that the heats of combustion of aliphatic compounds are slightly larger than those of the isomeric aromatic compounds.

T. H. P.

Applications of the Chronostiloscope. EUGENE VARENNE and L. GODEFROY (*Compt. rend.*, 1904, 138, 79—81).—The authors have calculated the value of n , the coefficient of internal friction of a liquid,

from the equation $n = \frac{\pi}{128000K'}$, where K' is the coefficient of viscosity of the liquid determined by their special form of constant pressure capillary viscosimeter [chronostiloscope], a sketch of which is given (compare this vol., i, 2).

The same instrument can also be used for the determination of the surface tension of a liquid, calculated by Tait's law from the weight p of the drops; the value of p being given by the equation $p = (V \times 60)/(nT) \times d$, T being the time in seconds taken for the volume V of the liquid to fall in drops at the rate of n drops per 60 seconds, and d the density of the liquid.

M. A. W.

Suspensions in Media of High Viscosity. ARTHUR MÜLLER (*Ber.*, 1904, 37, 11—16).—The following table shows the relationship between the viscosity of a solution and the "gold-number" as determined by Zsigmondy.

| | | Viscosity. | Gold-number. |
|----------------|---------------|------------|--------------|
| Gelatin | 0·5 per cent. | 1·443 | 0·005—0·01 |
| Glue | " | 1·213 | 0·005—0·01 |
| Casein | " | 1·182 | 0·01 |
| Albumin I | " | 1·052 | 0·15—0·25 |
| " II | " | 1·065 | |
| Gum [? arabic] | " | 1·082 | 0·15—4 |
| Gum tragacanth | " | 1·201 | about 2 |
| Wheat-starch | " | 1·043 | 4—6 |
| Dextrin | " | 1·028 | 6—20 |
| Potato-starch | " | 1·020 | 25 |
| Sucrose | " | 1·002 | ∞ |

With the exception of gum tragacanth and albumin, the gold-number increases steadily as the fluidity of the solution increases. The action of colloids in increasing the stability of suspensions of metallic gold is therefore due directly to their power of increasing the viscosity of the solution.

A similar result is found on attempting to precipitate the suspension by the addition of electrolytes; the colloidal solutions of high viscosity containing red phosphorus in suspension are only clarified with difficulty on adding sodium chloride. This is indicated by the following table, which shows the condition of the suspension after adding colloids of various kinds.

| Phosphorus suspension. | 10 per cent. NaCl solution. | Colloid. | After 24 hours. | After 48 hours. |
|------------------------|-----------------------------|----------------------|-----------------|-----------------|
| 50 c.c. | — | — | very turbid | very turbid |
| „ | 5 c.c. | — | clear | clear |
| „ | „ | 10 c.c. 0.5% gelatin | very turbid | very turbid |
| „ | „ | 5 c.c. 0.5% „ | turbid | turbid |
| „ | „ | 10 c.c. 0.5% dextrin | turbid | nearly clear |
| „ | „ | 10 c.c. 0.5% sucrose | scarcely turbid | clear |
| „ | „ | 10 c.c. 25% „ | very turbid | turbid |

The viscosity of the colloid thus protects the suspension both against gravitational and electrical forces. T. M. L.

Osmosis. A. GUILLEMIN (*Compt. rend.*, 1904, 138, 38—40).—It is usual to express the equilibrium attained in a Nernst osmometer in terms of the vapour tensions of the solvent and solution and the height to which the latter rises in the vertical tube. The author objects to this on the grounds (1) that it cannot be applied to all forms of osmometer, (2) that it does not indicate the real cause which maintains equilibrium. These difficulties are avoided by considering the “tension of expansibility” or the tendency of a liquid to give off vapour; equilibrium in an osmometer is reached when this tension is the same in the liquids on each side of the membrane. This point of view renders it unnecessary to regard a non-volatile solid as existing in solution as a perfect gas, instead there has only to be considered the internal vapour pressures of the solvent and solution of the substances. S. S.

Solubility of Gases in Liquids. I. LEONARDO CASSUTO (*Nuovo Cim.*, 1903, [v], 6, 5—20).—Measurements are given of the solubility of oxygen, hydrogen, nitrogen, and carbon monoxide in water under pressures ranging from 1—10 atmospheres. The gas was confined in a graduated glass tube connected by a thick-walled tube bent twice at right angles with a cylindrical bulb containing a known quantity of water kept agitated by a small soft iron stirrer controlled by a solenoid. The values given refer to Ostwald's coefficient of solubility $\lambda = V/v$, v denoting the volume of liquid which dissolves a volume V of gas

measured at the temperature and pressure of the experiment. It is shown that λ decreases in the case of hydrogen and oxygen at temperatures from 19.5—23.4° more rapidly than the pressure increases; in the case of nitrogen and carbon monoxide, the curves connecting λ and the pressure are more nearly straight lines, λ decreasing proportionately to the change of pressure. The values of λ under pressures near the atmospheric are practically constant at constant temperature, but with increasing temperature the solubility constant rapidly diminishes; thus, for hydrogen under atmospheric pressure, it changes from 0.01797 at 19.5° to 0.01728 at 23.4°. W. A. D.

Applicability of Nernst's Formula for a Mixture of Two Solvents. GABRIEL TIMOFÉEFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 646—648).—Nernst's formula for the osmotic pressure in mixtures of solvents (*Zeit. physikal. Chem.*, 1893, 11, 1) gives, for boric acid in acetic acid and water and for benzoic acid in acetic acid and benzene, results in moderately good agreement with the experimental ones.

T. H. P.

Isotonic Coefficients of Various Salts. GABRIEL TIMOFÉEFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 640—641).—The measurements were made with *Tradescantia discolor*, using de Vries's method, the following being the results:

| | Limits of concentration (gram-mols. per litre) of plasmolysed solution. | Isotonic coefficients taking i for carbamide as 1. |
|--------------------------|---|--|
| Ammonium chloride | 0.15 — 0.18 | 1.729 |
| „ bromide | 0.135 — 0.18 | 1.665 |
| „ iodide | 0.135 — 0.155 | 1.727 |
| Sodium chloride | 0.13 — 0.18 | 1.671 |
| „ bromide | 0.13 — 0.18 | 1.729 |
| „ nitrate | 0.13 — 0.145 | 1.793 |
| Potassium chloride | 0.14 — 0.175 | 1.732 |
| „ iodide | 0.12 — 0.16 | 1.949 |
| „ nitrate | 0.14 — 0.18 | 1.729 |
| Carbamide | 0.27 — 0.315 | [1.000] |

These results agree well with those obtained by de Vries and also with the values of i given by conductivity measurements. T. H. P.

Chemical Nature of Colloidal Solutions. JACQUES DUCLAUX (*Compt. rend.*, 1904, 138, 144—146).—When solutions of potassium ferrocyanide and a cupric salt are mixed, a complex ferrocyanide is formed, which, according to the proportion of the reagents, may remain in suspension or may coagulate and be precipitated, but in either case it contains potassium. The composition of the precipitate can be expressed by $K_nCu_mFeCy_6$, where $m + n/2 = 2$. The value of n depends on the amount of the cupric salt present, thus when cupric chloride is used it varies between 1.3° and zero, the latter value being

reached when the copper salt is in large excess. When a solution is made up so as to contain neither reagent in excess, the mean value of n is 0.4. It is found that the exact point of coagulation depends on the amounts taken. In the neighbourhood of the coagulation point, a slight change in the composition of the surrounding liquid produces a much larger effect on the colloid in equilibrium with it, so that the latter is very easily precipitated. The same effect can often be brought about by the addition of any salt of a polyvalent metal. S. S.

Rate of Formation of Iodates. E. L. C. FORSTER (*J. Physical Chem.*, 1903, 7, 640—651).—The author has extended the work of Schwicker on the rate of formation of iodate in alkaline solutions of iodine (Abstr., 1895, ii, 213). In Schwicker's experiments, the influence of the potassium iodide was neglected. The author finds that there is a great difference between the reactions in colourless and in brown solutions. In the former, that is, when the alkali is in excess, the rate is approximately proportional to the concentrations of the $\cdot\text{OI}$, the $\bar{\text{I}}$, and the HOI . In the latter, that is, when the iodine is in excess, the results are more complicated, and it could not be stated whether such proportionality exists. The rate of formation of iodate is, however, increased by increasing the concentration of the iodine or of the potassium hydroxide, but is decreased by increasing the concentration of the iodide. By continued increase of the potassium hydroxide, so that a colourless solution is ultimately obtained, the rate passes through a maximum. Experiments at 30.4° and at 0° indicate that the temperature coefficient is lower than the customary value.

L. M. J.

Action of Sodium and Potassium Amalgams on Various Aqueous Solutions. GUSTAVE FERNEKES (*J. Physical Chem.*, 1903, 7, 611—639).—The influence of various salts on the rate of liberation of hydrogen from water by magnesium has been investigated by Kahlenberg and others (Abstr., 1903, ii, 426). The author has extended this work by replacing the magnesium by sodium or potassium amalgam. The methods employed for measuring the volume of gas liberated at various intervals of time are described. A large number of salts and also of organic compounds were investigated. Most of the salts of inorganic acids cause retardation of the rate of liberation of the hydrogen. Acids and acid salts produce an acceleration, as do also most of the organic compounds examined; this was especially marked in the case of the hydrocarbons, although they are but slightly soluble in water, for example, paraffin, vaselin, hexane, heptane, &c. Sodium sulphite also accelerates the rate. The behaviour of sodium hydroxide was anomalous; specimens prepared from [sodium cause retardation, but those obtained by purification by alcohol cause a great acceleration. This the author ascribes to organic impurities, probably hydrocarbons, in the latter samples. He considers that the results are not capable of explanation by the dissociation theory, but that they may be explained on the basis of Kahlenberg's view of a chemical union between solvent and solute.

L. M. J.

Action of Emulsin. REGINALD O. HERZOG (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 332—339).—The velocity of emulsin or invertin action is determined by the equation:

$$k_1(1 - \epsilon) = \frac{1}{t} L \left(1 - \frac{\epsilon}{a} \right) / \left(1 - \frac{x}{a} \right),$$

where a is the concentration at the beginning, x the amount of sugar inverted in period t , k_1 the velocity constant of the reaction if taking place without autocatalysis, and k_2 the constant of the autocatalysis; $\epsilon = ak_2/k_1$. This formula is applied by the author to a number of cases studied by Henri.

A. McK.

Production of High Vacua without the Use of Mercury Pumps or Liquid Air. FRIEDRICH KRAFFT (*Ber.*, 1904, 37, 95—100).—Although small apparatus may be highly exhausted most conveniently by the use of mercury pumps, other methods are often desirable in the case of larger vessels. These may be exhausted by means of a water-pump, and filled four times with carbon dioxide, pumping out after each admission of gas. A 50 per cent. solution of potassium hydroxide is next introduced into a bulb connected with the apparatus, and the remaining carbon dioxide is thus rapidly absorbed. The water-vapour still present is condensed by cooling the potash-vessel with ice and salt, and finally with solid carbon dioxide and ether. The vacuum of the green cathode-light is thus reached in 15 to 30 minutes, even in the case of large vessels. When basic substances are being treated, ether or other vapours may be employed in place of carbon dioxide. A suitable arrangement of apparatus is described and figured.

C. H. D.

Hypotheses of Valency and the Course of Chemical Reactions. ARTHUR MICHAEL (*J. pr. Chem.*, 1903, [ii], 68, 487—520. Compare Abstr., 1900, i, 321).—A theoretical paper, in which the valency of an atom is considered as representing the resultant of the various chemical forces influencing the atom. The importance of the thermochemical study of organic reactions is maintained. The heat of formation of fatty isomerides, having a negative nucleus in common, is greater the greater the influence of positive hydrocarbon radicles on this nucleus. Many examples are discussed, and the views of Vorländer (*Abstr.*, 1902, ii, 250) and Thiele (*Abstr.*, 1899, i, 554) on unsaturated compounds are criticised. The conclusions arrived at are applied to the question of the constitution of benzene, phenol, quinone, and naphthalene, and to the formation of additive compounds.

A theory of the origin of matter from two primary substances is also suggested.

The paper does not lend itself to abstraction, and reference must be made to the original.

C. H. D.

Inorganic Chemistry.

Coefficient of Distribution of Hydrogen Peroxide between Water and Ether. K. OSIPOFF and S. POPOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 637—639).—The following table gives the results obtained at 17.5°:

| | | | | | | | | | |
|--|---------------|--------|-------|-------|-------|-------|-------|-------|-------|
| Vol. of ether : vol. of water | $\frac{1}{2}$ | 1 | 2 | 5 | 6 | 7 | 8 | 9 | 10 |
| Conc. of H_2O_2 in ether | 0.0575 | 0.0596 | 0.060 | 0.060 | 0.075 | 0.074 | 0.067 | 0.070 | 0.072 |
| Conc. of H_2O_2 in water | | | | | | | | | |

The distribution coefficients were also determined at 3° and 7°, and also the influence on them of sodium chloride and of sodium and potassium carbonates. The first of these produces no change in the coefficient, but both the carbonates cause a diminution in the solubility of hydrogen peroxide in ether. T. H. P.

The System Bromine + Iodine. H. W. BAKHUIS ROOZEBOOM (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 331—332).—The boiling points of liquid mixtures, from 100 per cent. bromine to 100 per cent. iodine, and the vapours yielded by those mixtures are diagrammatically represented. Indication is afforded that a compound is produced, possibly BrI . A. McK.

The Rendering Active of Oxygen. IX. Autoxidation of Cerous Salts. CARL ENGLER (*Ber.*, 1904, 37, 49—59. Compare *Abstr.*, 1903, ii, 599).—In presence of cerous salts, atmospheric oxygen is absorbed by arsenious acid, but only a single atom of oxygen is rendered active by a single atom of cerium, whilst Baur (*Abstr.*, 1903, ii, 729) found that 1.5 atoms were. The difference is not due to side-actions, as the experiments were carried out very rapidly, especially when cerous chloride was used in place of the sulphate. T. M. L.

Separation of Sulphur by the Incomplete Combination of Hydrogen Sulphide. A Lecture Experiment. JOSEF HABERMANN (*Zeit. anorg. Chem.*, 1904, 38, 101—106).—The incomplete combustion of hydrogen sulphide according to the equation $2\text{H}_2\text{S} + \text{O}_2 = 2\text{H}_2\text{O} + \text{S}_2$, is considered as the primary cause of the occurrence of sulphur in volcanic districts. An experiment is described in support of this view. A. McK.

Molecular Weight of Sulphur in Solution. GABRIEL TIMOFÉEFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 644—646).—The author has determined, by the ebullioscopic method, the molecular

weight, of octahedral sulphur dissolved in chloroform, carbon disulphide, or benzene. The means of the results are as follows:

In chloroform, molecular weight = 193 ($S_5 = 192$).

In carbon bisulphide, „ „ = 250 ($S_8 = 256$).

In benzene, „ „ = 151–313 ($S_8 = 160$; $S_9 = 288$ and $S_{10} = 320$). T. H. P.

Cryoscopic Observations on the Different Forms of Sulphur. S. F. POPOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 642–643).—The author has examined the cryoscopic behaviour of amorphous, octahedral, and prismatic sulphur in dimethylaniline and benzene. The results show that: (1) the associating power of dimethylaniline is the same as that of benzene. (2) All three modifications of sulphur exhibit identical behaviour. (3) The complexity of the molecules is directly proportional to the concentration. T. H. P.

[Tellurium Compounds.] **A Correction.** ALEXANDER GUTBIER and FERDINAND FLURY (*Zeit. anorg. Chem.*, 1904, 38, 256).—The authors had previously indicated (Abstr., 1903, ii, 71) that certain investigators find that telluric acid cannot be obtained free from an aquamarine blue tint, possibly due to chromic oxide. This statement ought, however, to refer not to telluric acid but to telluriodates (compare Weinland and Prause, Abstr., 1901, ii, 599). A. McK.

Researches on Phosphorus and Phosphoric Acids. HENRI GIRAN (*Ann. Chim. Phys.*, 1903, [vii], 30, 203–288).—An account of work already published (compare Abstr., 1902, ii, 318, 549; 1903, ii, 139, 197, 270, 362). The author gives details of experiments on the velocity of conversion of a solution of metaphosphoric into pyrophosphoric acid, and of pyrophosphoric into orthophosphoric acid; the former is a rapid and the latter a slow transformation. The values given in this paper for the heats of formation of the three phosphoric acids are slightly higher (0.01 to 0.11 Cals.) than those given in his former papers. M. A. W.

Formation of Arsenates from Arsenious Acid and Metallic Peroxides. O. SCHAIRER (*Chem. Zeit.*, 1904, 28, 15).—Sodium arsenate, lead arsenate, and barium arsenate are formed by the action of sodium peroxide, lead peroxide, and barium peroxide respectively on arsenious acid. A. McK.

Equilibrium of Gases in the Bunsen Flame. **Chemical Determination of Temperatures of Flames.** FRITZ HABER and F. RICHARDT (*Zeit. anorg. Chem.*, 1904, 38, 5–64).—By utilising the method of Smithells and Ingle (*Trans.*, 1892, 61, 204), the authors have determined the temperatures of Bunsen flames and compared their results with the constants obtained for the equilibrium of the gases involved. In the inner combustion zone, the equilibrium $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$ is very quickly attained, and is not appreciably altered when the gases are cooled. Accordingly, from the products of combustion in the inner zone, the temperature of the latter may be

directly estimated by means of the reaction isochores of the equilibrium.

The green light from the inner zone is a luminescence phenomenon; during the establishment of the equilibrium, a greater portion of the free energy is eliminated in the form of radiation of short wave-length than should be occasioned by the temperature alone.

Quantitative determinations of the gases of the inner zone were made, and the relationships of the various concentrations are given. The ratio $[\text{H}_2\text{O}]:[\text{CO}_2]=k$ was determined gravimetrically, whilst $[\text{CO}]:[\text{H}_2]=k'$ was determined volumetrically.

The equilibrium constant $K(=k.k')$ is the same, within the limit of experimental error, as that calculated from the results of Hahn (Abstr., 1903, ii, 274). The temperature of the combustion zone determined by thermoelectrical measurements is as high in value as that calculated from the composition of the gases from the reaction isochores. The results are almost the same when the temperature is calculated from the heats of combustion and the specific heats of the gases. The results quoted were obtained with temperatures varying from 1275° to 1500°.

A. McK.

Fractional Combustion of Gas Mixtures, containing Hydrogen, by Heated Palladium Wire. F. RICHARDT (*Zeit. anorg. Chem.*, 1904, 38, 65—91).—From a mixture of carbon monoxide and hydrogen, it is impossible to remove the hydrogen by combustion in such a manner that only carbon monoxide remains. The combustion of carbon monoxide in presence of heated palladium is complete at 300°. In presence of heated palladium wire, methane is not attacked by oxygen when the temperature does not exceed 450°. Above 450° and under a visible red heat, methane is attacked when it is in contact with the palladium wire for a sufficiently long time. When a current of methane and air is passed over palladium wire, there is little combustion even at 600—650°. The influence of hydrogen on the combustion of methane in presence of palladium has also been studied.

Ethane behaves like methane. A separation of the two gases by partial combustion is impossible. The separation of ethane or methane from hydrogen may, however, be effected by heated palladium wire.

Ethylene begins to burn at 300°.

A. McK.

Reduction of Alkali Iodates and Chlorates with Hydrazine Sulphate. MAX SCHLÖTTER (*Zeit. anorg. Chem.*, 1904, 38, 184—190).—Iodates and chlorates can be quantitatively reduced by hydrazine sulphate; the reduction with iodates is instantaneous, whilst that with chlorates is complete after the solution has been boiled for several hours. The changes are represented as follows: $5\text{N}_2\text{H}_4, \text{H}_2\text{SO}_4 + 4\text{HIO}_3 = 5\text{N}_2 + 12\text{H}_2\text{O} + 5\text{H}_2\text{SO}_4 + 4\text{I}$. The iodine, liberated in this manner, is then further reduced, thus $4\text{I} + \text{N}_2\text{H}_4 = 4\text{HI} + \text{N}_2$ (compare this vol., ii, 146).

A. McK.

Ammonia and Metallo-ammonium Bases. I. HANS EULER (*Arkiv Kem. Min. Geol.*, 1903, 1, i, 77—91. Compare Abstr., 1903, ii, 544 and 717).—None of the hypotheses put forward

in explanation of the transformation of tervalent into quinquevalent nitrogen—including those of Werner (Abstr., 1902, ii, 554), Hantzsch (Abstr., 1900, ii, 69), who introduces the idea of the hydration of the ions, Spiegel (Abstr., 1902, ii, 248), who brings forward the notion of "neutral affinities" produced by electrons, and Hinrichsen (Abstr., 1902, ii, 129)—is capable of treating this change in a quantitative manner.

According to the author's views, which are based on the ionic hypothesis and the law of mass action, the equilibrium between ammonia and ammonium hydroxide in aqueous solution is expressed by the equation: $k = K_{\text{water}} / (K_2 \cdot K_2')$, in which the constants K_2 and K_2' are determined by: $C_{\text{NH}_4}^+ \cdot C_{\text{OH}}^- = K_2 \cdot C_{\text{NH}_4\text{OH}}$ and $C_{\text{NH}_3}^+ \cdot C_{\text{H}}^+ = K_2' \cdot C_{\text{NH}_4}^+$. In this it is assumed that an atom of nitrogen can take up both positive and negative charges; but if the valency is considered as the action of electric charges, this is merely an expression of the fact that four positive atoms and one negative atom give, with one atom of nitrogen, a stable compound.

The above method of regarding change of valency may also be applied to the change of a double linking between carbon atoms into a single one, to the change of the degree of oxidation of a compound, for example, the conversion of cuprous into cupric oxide, &c. The following law, based on the above principles, is laid down by the author: *The compositions of all chemical compounds and molecular compounds must be regarded as a function of a force of valency (probably of an electrical nature) and also, as was done by van't Hoff, of the temperature and pressure (also of the solvent).* In other words: *The change of valency is due to the simultaneous splitting off of two oppositely charged ions in such quantities that their maximum dissociation product is exceeded.*

The author then gives the results of conductivity measurements of solutions of various bases in ammonia and in amines. The numbers obtained for silver oxide have already been given (*loc. cit.*). The new values arrived at are for zinc hydroxide in ammonia, cadmium hydroxide in ammonia, aluminium hydroxide in methylamine, and magnesium hydroxide in ammonia and methylamine. Concentration elements containing (1) ammoniacal and aqueous zinc sulphate solutions and (2) ammoniacal and aqueous cadmium sulphate solutions were also examined.

T. H. P.

Electrolytic Separation of Metals of the Alkaline Earths. ALFRED COEHN and WILHELM KETTEMBEIL (*Zeit. anorg. Chem.*, 1904, 38, 198—212).—Attempts were made to separate the metals of the alkalis and those of the alkaline earths by an electrolytic method. By fractional electrolysis, it was found possible to separate barium from magnesium. Saturated solutions of barium, strontium, and calcium chlorides were separately electrolysed and the results tabulated, showing the *E.M.F.*, the time required, and the yield in each case. The relationship between the yield and the *E.M.F.* is indicated; the latter was measured against a calomel electrode at 15—18°. The yields at first rapidly increase with the *E.M.F.* and then become smaller.

The differences representing the beginning of the amalgam formation with saturated solutions of the three metals are as follows :

Ba : Sr = 0.2, Sr : Ca = 0.25, and Ba : Ca = 0.45 volt.

A quantitative electrolytic separation of barium and strontium is possible when the barium concentration is large. Similarly, when a current of 0.08 ampere was passed for 2—3 hours, it was found possible to separate strontium from calcium.

A. McK.

Colloidal Properties of Calcium Fluoride. I and II. EMANUELE PATERNÒ and E. MAZZUCHELLI (*Atti R. Accad. Lincei*, 1903, [v], 12, ii, 420—428 and 520—528).—When a solution of calcium chloride is added to an excess of an alkali fluoride, an immediate precipitate of calcium fluoride is formed, but on adding the alkali fluoride to the calcium salt, only a slight turbidity is produced, which redissolves on stirring, leaving a slight opalescence. Using concentrated solutions, the solubility of the calcium fluoride is only temporary, and after a short time it is reprecipitated; but in dilute solutions, months may elapse without precipitation taking place. By dialysis, solutions containing 0.15—0.25 per cent. of colloidal calcium fluoride can be obtained; these cannot be concentrated by evaporating over a water-bath or at the ordinary temperature without calcium fluoride separating at the surface, but if the evaporation be effected in a vacuum over sulphuric acid, solutions containing as much as 2 per cent. of the solid can be prepared. These solutions are rapidly precipitated by alkalis and by acids, the rapidity of precipitation being proportional to the energy of the acid; neutral salts effect the same result more slowly, the rapidity being greatest in the case of the salts of heavy metals. By non-electrolytes, for instance methyl alcohol and acetone, the colloidal solutions are not precipitated. Alkali acetates, benzoates, and succinates rapidly cause coagulation, but citrates and tartrates only act in this way when present in excess.

When an excess of calcium chloride solution is mixed with a solution of potassium fluoride containing dissolved silver fluoride, the latter is usually precipitated as silver chloride, but on diminishing the relative amount of silver fluoride it becomes more and more difficult of precipitation, and ultimately the silver chloride remains dissolved in a colloidal form in the colloidal calcium fluoride solution. On adding any of the substances which precipitate the calcium fluoride, the silver chloride is also precipitated. Similar results are obtained with silver iodide.

An excess of a calcium salt in solution is necessary to enable calcium fluoride to exist in the colloidal form. In a solution containing $\text{CaCl}_2 : 2\text{KF}$, precipitation always occurs, although with varying rapidity, depending on the concentration, being greatest at greatest concentration. Using an excess of calcium chloride, the precipitation in concentrated solution is more rapid than when an excess is not employed, but in dilute solutions the precipitation is greatly hindered or entirely prevented. A theoretical explanation of these

facts is given, and the difference in the appearance of the precipitate formed under different conditions discussed.

In the precipitation of calcium fluoride from potassium fluoride by an equivalent of calcium chloride or acetate, the thermal change is not complete at once; for instance, the change $\text{KF} + \frac{1}{2}\text{CaCl}_2 + \text{aq} = \text{KCl} + \frac{1}{2}\text{CaF}_2(\text{insol.}) + \text{aq}$, which should give 2.2 Cal., after 40 seconds produces only 1.930 Cal., and after 400 seconds 2.134 Cal. in a solution containing 19 grams of fluorine in three litres. In more dilute solution, the development of heat is slower and less complete, corresponding with the greater amount of calcium fluoride held in solution. It is maintained, contrary to the usual views, that the precipitation of colloidal substances from solution may develop heat. The electrical conductivity of solutions at the same dilution which have been prepared by different methods, but yet contain the same quantities of the components of the equation, $\text{CaCl}_2 + 2\text{KF} = \text{CaF}_2 + 2\text{KCl}$, is always constant, although in some cases the whole of the calcium fluoride has been precipitated and in others a portion remains dissolved; it is thus seen that the dissolved calcium fluoride is not ionised, but exists in the molecular state. It is noteworthy that the colloidal solutions of calcium fluoride are always more or less opalescent, probably corresponding with a state of minute suspension of the solid.

W. A. D.

The Fluorochlorides, Fluorobromides, and Fluoriodides of the Alkaline Earth Metals. EDOUARD DEFAQZ (*Compt. rend.*, 1904, 138, 197—199. Compare this vol., ii, 123).—*Barium fluorochloride*, prepared by heating 10 parts of manganese fluoride and 40 parts of barium chloride for two hours at 1000° , and purified by repeated extraction with cold water and finally with alcohol at 95° , crystallises in colourless, transparent plates and has a sp. gr. 4.51 at 18° ; it is insoluble in, and undecomposed by, boiling alcohol, very slowly decomposed by cold, but much more readily attacked by the boiling solvent, being thereby converted into the chloride and fluoride of barium; dilute acetic, hydrochloric, or nitric acid effects a similar decomposition; it is soluble in concentrated hydrochloric or nitric acids, whilst hot sulphuric acid decomposes it into barium sulphate, hydrofluoric and hydrochloric acids. It is not changed by fusion with manganese chloride, but converted into barium fluoride on fusion with barium chloride.

Barium fluorobromide, $\text{BaF}_2 \cdot \text{BaBr}_2$, has a sp. gr. 4.96, and *barium fluoriodide*, $\text{BaF}_2 \cdot \text{BaI}_2$, a sp. gr. 5.21; the preparation and properties of these two compounds are identical with those of the fluorochloride, but they are more readily dissociated by water.

M. A. W.

Preparation of Salts by Double Decomposition. WILHELM MEYERHOFFER (*Ber.*, 1904, 37, 261—265).—Referring to the preparation of barium nitrite by double decomposition of barium chloride and sodium nitrite described by Witt and Ludwig (this vol., ii, 124), the general laws underlying such changes are discussed, and it is pointed out that under the conditions of Witt and Ludwig's experiments the salt pair $\text{Ba}(\text{NO}_3)_2 + \text{NaCl}$ is stable, within its interval of change, and that in presence of water it will separate as a third salt barium

chloride, sodium nitrite remaining in solution. To prevent this separation, the addition of excess of sodium nitrite is necessary.

E. F. A.

Preparation of Barium Nitrite. OTTO N. WITT and KURT LUDWIG (*Ber.*, 1904, 37, 382—384. Compare this vol., ii, 124).—Polemical, a reply to Meyerhoffer's criticisms (preceding abstract). E. F. A.

Radium. WILHELM MARCKWALD (*Ber.*, 1904, 37, 88—91).—*Separation of Radium from Barium.*—On adding a concentrated aqueous solution of radium barium chloride to 1 per cent. sodium amalgam, part of the sodium in the amalgam is displaced by an equivalent quantity of radium and barium, the proportion of radium absorbed being greater than that of barium; on decomposing the amalgam with hydrochloric acid, the metallic chloride obtained is much more active than the original salt. By repeating this process, a much enriched salt is obtained, but the manipulation is tedious, and the method offers little advantage over the ordinary one of fractional crystallisation.

Phosphorescence of Anhydrous Radium Barium Chloride.—It is known that anhydrous radium barium chloride exhibits phosphorescence whilst the hydrated salt fails to do so; this is due to anhydrous barium chloride showing phosphorescence with the Becquerel rays, whereas the hydrated salt is not affected.

Induced Radioactivity.—On immersing strips of various metals in a freshly-prepared solution of radium barium chloride, after 15—30 minutes they show a maximum induced radioactivity; on exposure to the air, the activity during the course of a day gradually dies away. Different metals show a different induced activity, the order, commencing with that which shows the greatest, being magnesium, tin, copper, silver, bismuth, palladium. As a rule, on dipping different strips of the same metal successively in the same solution, the inductive effect of the latter hardly changes; with magnesium, however, the second strip shows practically no induced activity, owing to a slight alkalinity imparted to the solution. On adding a drop of acid to the solution, a continuously inductive product is obtained. That the action of acid does not depend merely on its dissolving a film of oxide from the metal is shown by the fact that a solution containing ammonium chloride, which would effect this result, is not inductive. Similar results are obtained with zinc, but copper in presence of either acid or alkali becomes radioactive.

W. A. D.

The Equilibrium $\text{Mg}(\text{OH})_2 + 2\text{NH}_4\text{Cl} = \text{MgCl}_2 + 2\text{NH}_4\text{OH}$. WALTER HERZ and G. MUHS (*Zeit. anorg. Chem.*, 1904, 38, 138—141).—The fact that magnesium salts give no precipitate with ammonia in the presence of ammonium salts follows, according to Lovén, as a consequence of the law of mass action without the hypothesis of complex compounds. The equilibrium $\text{Mg}(\text{OH})_2 + 2\text{NH}_4\text{Cl} = \text{MgCl}_2 + 2\text{NH}_4\cdot\text{OH}$ has now been experimentally examined. According to the law of mass action, the equation follows $[\text{Mg}^{++}]^{1.5}/[\text{NH}_4] = \sqrt{K_1/4K_2z} = K$, where $K_1 = [\text{Mg}^{++}][\text{OH}']^2$ and $K_2 = [\text{NH}_4'][\text{OH}']$.

Magnesium hydroxide was agitated with an aqueous solution of ammonium chloride at 29°, allowed to subside, and the free ammonia titrated in an aliquot portion with nitrophenol as indicator. The constants 0.159, 0.140, 0.154, 0.152, and 0.141 were obtained. The results with ammonium nitrate were not quite so concordant.

A. McK.

Peroxides of Zinc. ROBERT DE FORCRAND (*Compt. rend.*, 1904, 138, 129—131).—Polemical. A reply to Kuriloff (this vol., ii, 36).

S. S.

Influence of the Physical Nature of the Anode on the Constitution of Lead Peroxide Deposited by Electrolysis. AUGUSTE HOLLARD (*Compt. rend.*, 1904, 138, 142—144. Compare Abstr., 1903, ii, 294).—Usually the peroxide of lead deposited by electrolysis varies in composition according to the strength of the solution taken. It is shown that if the anode is made of platinum roughened by a sand blast, a peroxide of constant composition can be obtained.

S. S.

Lead Salt Solutions Sensitive to Light. KARL A. HOFMANN and V. WÖFLER (*Ber.*, 1904, 37, 249—252).—Lead haloids in dilute sodium thiosulphate solutions are observed under the influence of light to deposit a red precipitate, whereas in diffused light or in the dark, black lead sulphide is formed. In the case of lead chloride, a polysulphide, $Pb_4S_6Cl_2$, is formed, whereas with the iodide, a copper-red powder, $Pb_3S_4I_2$, is the product; this can also be prepared by the action of yellow ammonium sulphide solution on lead iodide.

E. F. A.

Constitution of the Copper-Tin Series of Alloys. CHARLES T. HEYCOCK and FRANCIS H. NEVILLE (*Phil. Trans.*, 1903, A, 202, 1—69).—Details are given of work already described (Abstr., 1901, ii, 508; 1902, ii, 261).

J. C. P.

Non-precipitation of Copper by Hydrogen Sulphide in the presence of Potassium Cyanide. FREDERICK P. TREADWELL and C. VON GIRSEWALD (*Zeit. anorg. Chem.*, 1904, 38, 92—100).—The salts $[Cu_2(CN)_8H_2O]K$ and $[Cu_2(CN)_4]K_2$ are readily decomposed by hydrogen sulphide, copper sulphide being formed, whilst the salt $[Cu_2(CN)_8]K_6$ is not acted on in the solid state or in concentrated solution. The authors come to the conclusion that the non-precipitation of copper by hydrogen sulphide in the presence of potassium cyanide is due to the formation of ions containing more cyanogen than $[Cu_2(CN)_4]$, such as $[Cu_2(CN)_8]$ or possibly $[Cu_2(CN)_6]$.

W. P. S.

Amalgams. WILHELM KETTEMBEIL (*Zeit. anorg. Chem.*, 1904, 38, 213—231. Compare this vol., ii, 165).—Three classes of amalgams are described. Firstly, the two first groups of the periodic system form amalgams so stable that they can be separated even from aqueous solutions. In the second class are included the two next groups together with boron, carbon, silicon, aluminium, and the rare earths,

which form amalgams, which cannot be separated from aqueous solutions. Other metals form amalgams of the third class. When solutions of the rare earths are electrolysed with mercury cathodes, there is no formation of amalgam at the cathode. According to Nernst, a complex ion, MH_2 , separates during the electrolysis of alkali salts at about 1.4 volt cathodic potential. Above this point, with one-third of the current, the formation of amalgam should occur. Below this point to that where the metal ion itself separates, no formation of amalgam could be attained, even in a freezing mixture, but evolution of hydrogen took place. It is supposed that the amalgam is formed, but is decomposed with such rapidity as to escape detection. The breaks in the decomposition potential curves observed during the electrolysis of sodium, barium, and magnesium with platinum cathodes above that of hydrogen are in the same position when mercury cathodes are employed.

Sodium amalgam forms a potassium amalgam when immersed in potassium hydroxide solution; sodium amalgam can, however, be prepared from potassium amalgam and sodium hydroxide solution.

A. McK.

Action of Radium Rays on Mercurous Salts. SIDNEY SKINNER (*Proc. Camb. Phil. Soc.*, 1904, 12, 260—261).—Mercurous sulphate darkens rapidly on exposure to light, and it has been shown that this result is due chiefly to the ultra-violet rays, and is independent of the presence of air. The rays from radium bromide have a similar effect, the mercurous salt phosphorescing very slightly under the action of the rays. The author does not favour the view that the darkening is due to the production of mercury and mercuric salt. It is suggested that a dark sub-salt may be formed, or that a polymeric modification may be produced. In any case, the action is so small that its effect on the *E.M.F.* of a Clark cell is negligible.

J. C. P.

Determination of the Atomic Weight of Rare Earths. WILHELM WILD (*Zeit. anorg. Chem.*, 1904, 38, 191—197).—In order to determine the atomic weight of a mixture of rare earths of the didymium and yttrium group by a volumetric method, the author dissolves 0.1 gram of the oxide in 30—40 c.c. *N*/10 sulphuric acid, precipitates as oxalate with 5 c.c. of a solution of neutral potassium oxalate (1 : 5), and then titrates the excess of acid with *N*/10 sodium hydroxide solution using phenolphthalein as indicator. For a gravimetric determination of the atomic weight, the oxide is dissolved in hydrochloric acid and then converted into sulphate by sulphuric acid, the product being subsequently heated at 450—500° and quickly weighed to prevent absorption of moisture.

A. McK.

Use of Bismuth as a Separating Agent in the Series of the Rare Earths. GEORGES URBAIN and HENRI LACOMBE (*Compt. rend.*, 1904, 138, 84—85).—By an extension of the method employed for the separation of samarium and gadolinium (compare this vol., ii, 37) to large quantities of the rare earth oxides, the authors have effected

the separation of gadolinium and Demarçay's europium which must thus be regarded as the first term of the yttrium earth series.

A new method of separating the elements of the rare earths is described, based also on the isomorphism of the double nitrates of magnesium and the rare earths and bismuth magnesium nitrate; after the removal of the least soluble rare earth salt by fractional crystallisation, the more soluble rare earth salt is carried down mechanically in a state of purity on the addition of a further quantity of bismuth magnesium nitrate to the uncrystallisable mother liquor. By this method, gadolinium can be separated from crude yttrium earths, which are much less rich in this element than are the xenotime earths.

M. A. W.

New Method for the Separation of Rare Earths. I. Preparation of Pure Neodymium Oxide. OTTO HOLMBERG (*Bihang K. Svenska Vet.-Akad. Handl.*, 1902—1903, 28, ii, No. 5, 1—53).—The author has prepared the thorium, cerium, lanthanum, didymium, yttrium, and praseodymium salts of the following acids, and has determined their solubilities in water and in some cases in solutions of the corresponding acids and of their ammonium salts: tartaric, malonic, citric, benzenesulphonic, *m*-nitrobenzenesulphonic, *m*-chlorobenzenesulphonic, *m*-bromobenzenesulphonic, 3-nitro-6-chlorobenzene-sulphonic, α -naphthalenesulphonic, 5:1-, 5:2-, and 8:2-nitronaphthalenesulphonic acids. His results show that the salts best suited as a means of separation of the rare earths are the *m*-nitrobenzenesulphonates, which not only show considerable differences of solubility among themselves, but also vary greatly in solubility with the temperature; they are also easily separated from the mother liquor and crystallise with the same amount of water, namely, $6\text{H}_2\text{O}$, excepting in the case of the thorium and yttrium salts, which contain $7\text{H}_2\text{O}$; further, the *m*-nitrobenzenesulphonates of the yttrium earths, gadolinium, and samarium are not isomorphous with those of the cerite metals.

From a didymium material similar to that used by Bodman (*Bihang K. Svenska Vet. Akad. Handl.*, 1900, 26, ii, No. 3; Abstr., 1902, ii, 507), which contains neodymium, praseodymium, and samarium, and gives an atomic weight of 142.4, the author has succeeded in obtaining neodymium oxide quite free from praseodymium and samarium. Two hundred grams of the oxide were dissolved in *m*-nitrobenzenesulphonic acid and the solution submitted to a series of systematic crystallisations, by which means 12 fractions were obtained; these then underwent further fractionation. Twenty-three crystalline fractions were thus ultimately obtained, and of these the first few were found to contain samarium, whilst the next were constituted of pure neodymium salt and gave the atomic weight 143.6. The later fractions contained increasing quantities of praseodymium.

T. H. P.

Separation of the Final Monazite Fractions. Preparation of Pure Gadolinium Oxide. ROBERT MARC (*Zeit. anorg. Chem.*, 1904, 38, 121—131).—The material employed for the preparation of pure gadolinium oxide consisted of the final chromic acid fractions from several kilograms of monazite. By treatment with potassium sul-

phate, this was sub-divided into fractions containing yttrium, erbium, terbium, and gadolinium on the one hand, and neodymium and samarium on the other. By aid of ammonia, a further fractionation was so conducted that in one portion no erbium, and in another no neodymium nor samarium, was visible; gadolinium was present in the fraction containing no erbium. Details of the separation are given. Finally, gadolinium oxide was obtained, which, after being strongly heated, still had a faintly yellow colour, which disappears when the oxide is heated in a current of hydrogen.

Samarium oxide and neodymium oxide were also separated and examined spectroscopically. Preparations rich in terbium were also obtained. A. McK.

Sulphates of Quadrivalent Cerium. RICHARD J. MEYER and ARTHUR AUFRECHT (*Ber.*, 1904, 37, 140—153).—Hot concentrated sulphuric acid converts pure ignited cerium dioxide, without dissolving it, into *anhydrous cerium sulphate*, $\text{Ce}(\text{SO}_4)_2$, no reduction taking place. The salt is washed free from sulphuric acid by glacial acetic acid and dried in a vacuum-desiccator over potassium hydroxide, and is then a deep yellow, crystalline powder. Water dissolves it at first extremely slowly, more quickly on warming, but when solution has once begun, almost unlimited quantities may be dissolved. The brown solution deposits basic salt on warming. The behaviour of ceric sulphate resembles that of ferric sulphate, and suggests that hydration or depolymerisation precedes solution. Acidified solutions deposit the known hydrated salt, $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, on evaporation.

If ceric sulphate be overheated, or if water be present in the sulphuric acid used, reduction takes place, oxygen and ozone being evolved, and the solution deposits long, golden, glistening needles of *cerosceric hydrogen sulphate*, $\text{Ce}_2\text{H}(\text{SO}_4)_4 \cdot 13\text{H}_2\text{O}$, which dissolves in water, readily forming a supersaturated solution. On recrystallising from very dilute sulphuric acid, partial reduction to the cerous state takes place. The formulæ obtained by Mendeléeff and Muthmann and Stützel (*Abstr.*, 1900, ii, 544) are to be thus accounted for. When ceric and cerous sulphates are mixed, a yellow, slimy substance is obtained, probably identical with the product of the decomposition of cerosceric sulphate by water.

Sulphurous acid reduces a solution of ceric sulphate in sulphuric acid, and the cerosceric hydrogen sulphate may be obtained in good crystals from the solution. Hydrogen peroxide also reduces ceric sulphate but cannot be applied quantitatively, as the reduction proceeds much further than is indicated by the reaction, probably from a catalytic decomposition of the hydrogen peroxide.

The analytical results of former authors are also compared, and are shown to be consistent with the above formulæ. C. H. D.

Separation of Praseodymium. C. R. BÖHM (*Zeit. angew. Chem.*, 1903, 16, 1220—1224).—An historical survey of the chemistry of praseodymium is first given.

The author submitted a mixture of didymium sulphate and potassium

nitrate to fractional crystallisation, whereby the separation into praseodymium and neodymium was indicated. One component of praseodymium, designated as Pr^a , possesses two bands, λ 596.6 and 589.6. The characteristic bands of the second component, Pr^b , are λ 481.1 and 444.0, whilst λ 469.0 is characteristic for Pr^γ (which Krüss terms *Di η*).
A. McK.

Holmium. SVEN FORSLING (*Bihang K. Svenska Vet. Akad. Handl.*, 1902—1903, 28, ii, No. 1, 1—21).—The author has examined the absorption spectra of solutions of different strengths of various fractions of rare earth oxides containing holmium and erbium, and gives the detailed results of the measurements. The methods used for the separation were: (1) fractionation of the chloride from hydrochloric acid solution and (2) fractionation of the dry chloride by allowing it to deliquesce and removing the liquid portion, the crystals remaining being then dried and again allowed to deliquesce and so on.

The results confirm the conclusion previously arrived at by the author that holmium is not an elementary substance, but a mixture of several components, to which correspond the different absorption bands. It appears probable that the "old" holmium consists not only of dysprosium with its two components, but that at least four other components are present.
T. H. P.

Some Compounds of the Chlorides and Fluorides of Aluminium. E. BAUD (*Ann. Chim. Phys.*, 1904, [viii], 1, 8—72).—This paper is principally a *résumé* of work already published (compare *Abstr.*, 1900, 369; 1901, ii, 161, 224, 303; 1902, ii, 142, 505; 1903, ii, 150, 214), and, in addition, the preparation and thermochemical properties of some new compounds are given: (1) With ammonia, $\text{Al}_2\text{Cl}_6 \cdot 2\frac{1}{3}\text{NH}_3$ is a colourless solid, distils without decomposition, and its heat of formation is +77.66 Cal.; $\text{Al}_2\text{Cl}_6 \cdot 6\text{NH}_3$ has a heat of formation +167.54 Cal. (2) With hydrogen sulphide; $\text{Al}_2\text{Cl}_6 \cdot 2\text{H}_2\text{S}$, dissociates at -45° . (3) With sulphur dioxide; $\text{Al}_2\text{Cl}_6 \cdot \text{SO}_2$, prepared by the direct union of aluminium chloride and sulphur dioxide at the ordinary temperature, distils at 200° , and its heat of solution is +150.54 Cal. at 15° , and heat of formation +18.33 Cal.; $\text{Al}_2\text{Cl}_6 \cdot 2\text{SO}_2$, prepared by the prolonged action of sulphur dioxide on the preceding compound, or by the action of liquid sulphur dioxide on aluminium chloride, or by subliming the chloride in a current of the gas, is a pasty mass, dissociates at 80° , losing sulphur dioxide, to form $\text{Al}_2\text{Cl}_6 \cdot \text{SO}_2$; its heat of solution is +149.31 Cal., and its heat of formation +28.93 Cal. (4) With metallic chlorides; $\text{Al}_2\text{Cl}_6 \cdot 2\text{AgCl}$, prepared by heating the two constituents in a sealed tube at 300° , is much less stable than the corresponding compounds with the alkali chlorides; its heat of solution is +151.45 Cal. at 22° , and its heat of formation +5.01 Cal.; $\text{Al}_2\text{Cl}_6 \cdot 1.5\text{CaCl}_2$, melts below 300° ; its heat of solution is +173.4 Cal. at 16° , and its heat of formation +9.28 Cal.; $\text{Al}_2\text{Cl}_6 \cdot 1.5\text{SrCl}_2$, melts below 300° ; its heat of solution is +164.39 Cal. at 19° , and its heat of formation +8.71 Cal.; $\text{Al}_2\text{Cl}_6 \cdot \text{BaCl}_2$, melts at 290° , and crystallises in silky scales resembling some specimens of natural spinel; its heat of formation is +5.29

Cal.; when heated at 500° , it loses aluminium chloride and forms $\text{Al}_2\text{Cl}_6, 1.5\text{BaCl}_2$, the heat of formation of which is $+7.30$ Cal.; $\text{Al}_2\text{Cl}_6, 1.5\text{ZnCl}_2$, is a pasty, translucent mass, less stable than the preceding compounds; its heat of solution is $+187.99$ Cal. at 15° , and its heat of formation is negative.

The double alkali chlorides, $\text{Al}_2\text{Cl}_6, 2\text{MCl}$, absorb ammonia to form compounds of the type $\text{Al}_2\text{Cl}_6, 2\text{MCl}, 12\text{NH}_3$; the heat of solution of the sodium compound is $+11.23$ Cal. and the heat of formation $+255.87$ Cal.; the corresponding values for the ammonium compound are -5.47 Cal. and $+252.08$ Cal., and for the potassium compound -6.08 Cal. and $+252.19$ Cal.

M. A. W.

Indium. ALFRED THIEL (*Ber.*, 1904, 37, 175—176. Compare C. Renz, this vol., ii, 149, and A. Sachs, *ibid.*, 38).—Indium has been prepared by the electrolysis of solutions of pure salts. It has a sp. gr. 7.12 at $13^{\circ}/4^{\circ}$, and its melting point, determined by different methods, is 155° .

Analyses of the pure sublimed trichloride give 115.08 ± 0.03 as the atomic weight, and this value has been confirmed by experiments with the bromide and oxide [details and standard not given]. The oxide forms glistening rhombohedra with the colour of chlorine. The *sulphide*, In_2S_3 , is a scarlet-red powder with a high metallic lustre, and the *monosulphide*, In_2S , is volatile, and forms a blackish-brown powder or minute yellowish-brown crystals. The *fluoride*, $\text{InF}_3, 3\text{H}_2\text{O}$, forms glistening crystals, is strongly doubly refractive, moderately soluble, and readily decomposed. The *oxychloride*, InOCl , is a sparingly soluble white powder. The *bromides*, InBr and InBr_2 , resemble the chlorides. Indium separated electrolytically has a colour between that of silver and platinum; platinum cathodes are attacked as the metal alloys with indium. The pure metal is extremely soft, and may be obtained in the form of wire by the aid of a sodium press. J. J. S.

Atomic Weight of Iron. II. Analysis of Ferrous Bromide. GREGORY P. BAXTER (*Zeit. anorg. Chem.*, 1904, 38, 232—245).—Ferrous bromide was prepared by heating iron in a current of dry nitrogen and hydrogen bromide at a temperature sufficient for the sublimation of the ferrous bromide. The sublimate was heated for a considerable time in a current of dry nitrogen and hydrogen bromide until it showed no trace of ferric salt when tested with ammonium thiocyanate. The salt, prepared in this manner, is stable in dry air; its colour varies from light yellow to dark brown.

The ferrous bromide was first oxidised by potassium dichromate and sulphuric acid, silver nitrate was then added to the solution, and the resulting silver bromide filtered off in a Gooch crucible, heated at 200° in an electrical oven, and then weighed. As a mean of four determinations, in two of which the silver obtainable from the bromide was also weighed, the value obtained for the atomic weight of iron was 55.857 ($\text{O} = 16$), being somewhat smaller than that obtained by the analysis of ferric oxide, which was 55.883 ($\text{O} = 16$). The value 55.88 ($\text{O} = 16.000$) may accordingly be taken for the atomic weight of iron.

Ferrous bromide has the sp. gr. 4.636 at $25^{\circ}/4^{\circ}$.

A. McK.

Pulverisation of "Nickel Grains" in Fuming Nitric Acid. W. A. HOLLIS (*Proc. Camb. Phil. Soc.*, 1904, 12, 253—259).—When a nickel grain is dropped into fuming nitric acid, the metal may be violently attacked, or it may become passive, or it may be slowly disintegrated, yielding a greyish-white powder with a dull metallic lustre. The powder is not pyrophoric, but is strongly magnetic. The disintegration is accompanied by slight chemical action, gaseous bubbles are formed, and the liquid becomes green. Evidence of pulverisation was obtained also on treating nickel "shot" in a similar manner. J. C. P.

Tungsten Compounds. EMIL SCHAEFER (*Zeit. anorg. Chem.*, 1904, 38, 142—183).—According to Hallopeau (*Abstr.*, 1899, ii, 32, 555), two potassium tungsten bronzes exist having the composition $K_2W_3O_9$ and $K_2W_5O_{15}$ respectively, whilst the compound isolated by Knorre is represented as $K_2W_4O_{12}$. Hallopeau's results are criticised, and it is experimentally shown that they are incorrect. Potassium tungsten bronze, prepared by fusing together a mixture of potassium carbonate and tungstic acid and then reducing the mass by coal gas or hydrogen, gave on analysis values corresponding with the formula $K_2W_4O_{12}$. The same bronze is also obtained when the molten mixture of potassium carbonate and tungstic acid is reduced by zinc.

Negative results were obtained when attempts were made to prepare thallium tungsten bronze. No definite compound was obtained from rubidium carbonate and tungstic acid.

Rubidium pentatungstate, $Rb_2W_5O_{16}$, prepared from rubidium oxide (1 part) and tungstic oxide (3—3.5 parts), forms glistening, rectangular leaflets. *Rubidium octatungstate*, $Rb_2W_8O_{25}$, was obtained in admixture with some bronze. *Thallium paratungstate* probably has the composition $5Tl_2O, 12WO_3$; prepared from sodium paratungstate and thallous sulphate, it forms a white, amorphous precipitate. *Rubidium paratungstate*, $5Rb_2O, 12WO_3, 18H_2O$, forms white, rhombic leaflets.

When an aqueous solution of normal sodium tungstate, Na_2WO_4 , is electrolysed in a cell where the electrodes were separated by a diaphragm, sodium paratungstate, $5Na_2O, 12WO_3$, is formed so long as the liquid in the neighbourhood of the anode reacts alkaline; as the electrolysis proceeds, the liquid at the anode gradually becomes neutral and then acid, and at the latter stage, sodium metatungstate, $Na_2W_4O_{13}$, is formed. Finally, tungstic acid hydrate is formed at the anode and sodium hydroxide at the cathode. The electrolysis of potassium tungstate proceeds in an analogous manner. When ammonium tungstate is used, the decomposition is complicated owing to rise of temperature and endosmosis taking place, but the results are on the whole analogous to those obtained with the alkali tungstates (compare Engels, this vol., ii, 129).

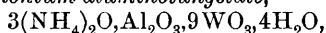
A. McK.

Derivatives of Complex Inorganic Acids. III and IV. ALLEN ROGERS and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1903, 25, 1223—1227, 1227—1229).—The following salts have been prepared

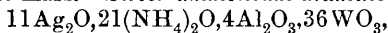
and analysed. *Ammonium silicovanadosophosphotungstate*, *ammonium titanovanadosophosphotungstate*, *ammonium zirconovanadosophosphotungstate*, *ammonium thorovanadosophosphotungstate*, and *ammonium stannivanadosophosphotungstate*. These salts separate from a concentrated, aqueous solution in large, brilliant black, octahedral crystals; their reactions with solutions of various acids, alkalis, and salts are described; although concordant results are obtained on analysis, the formulæ deducible from them are very complex; further work is therefore being undertaken on the subject.

Ammonium vanadosotungstate, $3(\text{NH}_4)_2\text{O} \cdot \text{V}_2\text{O}_5 \cdot 8\text{WO}_3 \cdot 10\text{H}_2\text{O}$, is a crystalline salt which is very soluble in water. *Ammonium vanadicosotungstate*, $5(\text{NH}_4)_2\text{O} \cdot 2\text{V}_2\text{O}_5 \cdot 14\text{WO}_3 \cdot 13\text{H}_2\text{O}$, forms black, well-defined, octahedral crystals and is very soluble in water. The behaviour of the salts with various reagents is described. E. G.

Derivatives of Complex Inorganic Acids. V. CLARENCE W. BALKE and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1903, 25, 1229—1234).—*Ammonium aluminotungstate*,



is obtained as a dense, highly refractive syrup which, on drying, forms a semi-transparent mass. *Silver ammonium aluminotungstate*,



is a yellow, crystalline salt, insoluble in water. *Ammonium bismuthotungstate*, $3(\text{NH}_4)_2\text{O} \cdot 2\text{Bi}_2\text{O}_3 \cdot 11\text{WO}_3 \cdot 10\text{H}_2\text{O}$, is obtained as an oil which, when dry, forms a yellow, transparent, vitreous mass. The corresponding *potassium* salt, $3\text{K}_2\text{O} \cdot 2\text{Bi}_2\text{O}_3 \cdot 11\text{WO}_3 \cdot 15\text{H}_2\text{O}$, separates as an oil which, on drying, yields a transparent, pale yellow, vitreous mass. The *strontium* salt, $3\text{SrO} \cdot 2\text{Bi}_2\text{O}_3 \cdot 11\text{WO}_3 \cdot 11\text{H}_2\text{O}$, is obtained as an oil which, on cooling, solidifies to a wax-like mass; when dried at 100° , it forms a hard yellow, vitreous mass and is insoluble in water. An account is given of the action of various reagents on these salts. E. G.

Pyrophoric Bismuth. PAUL THIBAUT (*Bull. Soc. chim.*, 1904, [iii], 31, 135—137).—See this vol., i, 247.

Crystallised Polysulphides of the Heavy Metals. KARL A. HOFMANN and F. HÖCHTLEN (*Ber.*, 1904, 37, 245—249. Compare Abstr., 1903, ii, 728).—*Gold ammonium polysulphide*, AuS_3NH_4 , is obtained in glistening, yellow, flat, rhombic prisms on allowing a mixture of aqueous gold chloride and ammonium polysulphide to remain for several days at a temperature of 5° . In absolute ethereal solution, gold chloride gives a dark brown precipitate of *auric sulphide*, Au_2S_3 . *Iridium ammonium pentadecasulphide*, $\text{IrS}_{15}(\text{NH}_4)_3$, crystallises in large, brown, octahedral crystals of the tetragonal system [$a : b = 0.915 : 1$].

Palladium ammonium undecasulphide, $\text{PdS}_{11}(\text{NH}_4)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$, crystallises in yellowish-red, glistening needles. Bismuth chloride forms with ammonium polysulphide a compound crystallising in glistening, black prisms which contains oxygen, and probably has the constitution $\text{S}_2[\text{Bi}(\text{S}_2\text{O}_3\text{NH}_4) \cdot \text{S}_4\text{NH}_4]_2$. E. F. A.

Colloidal Metals of the Platinum Group. I. CARL PAAL and CONRAD AMBERGER (*Ber.*, 1904, 37, 124—139).—The method employed to prepare colloidal solutions of silver, gold, &c., by means of protalbic and lysalbic acids (*Abstr.*, 1902, i, 653; ii, 500, 503, 508) may be extended to the platinum metals. A solution of chloroplatinic acid is added to an alkaline solution of sodium lysalbate or protalbate, and an excess of hydrazine hydrate is then added. The salts produced are removed by dialysis and the remaining liquid is concentrated on the water-bath, and finally in a vacuum. The product, dried at 100°, forms black, glistening scales dissolving readily in water to a dark brown, opalescent solution. Acetic acid precipitates the platinum, but the product rapidly passes into the insoluble modification. Electrolytes precipitate the hydrosol from its solutions without formation of the hydrogel. Colloidal preparations of palladium are obtained in similar manner, and have similar properties. Colloidal iridium is prepared by employing sodium amalgam as the reducing agent, or by passing gaseous hydrogen through the heated solution of sodium lysalbate and iridium chloride. The product resembles those from platinum and palladium, but has a much weaker catalytic action on hydrogen peroxide.
C. H. D.

Platinic Acid. ITALO BELLUCCI (*Atti R. Accad. Lincei*, 1903, [v], 12, ii, 635—642. Compare Miolati and Bellucci, *Abstr.*, 1900, ii, 732; 1901, ii, 246; Bellucci, *Abstr.*, 1902, ii, 267; 1903, ii, 155).—The hydrated platinic oxide, $\text{PtO}_2 \cdot 4\text{H}_2\text{O}$, is probably the acid $\text{Pt}(\text{OH})_6\text{H}_2$, corresponding with chloroplatinic acid, H_2PtCl_6 ; on dissolving it in aqueous sodium or potassium hydroxide and slowly evaporating the yellow solution obtained on the water-bath, crystals of the salts, $\text{Pt}(\text{OH})_6\text{Na}_2$ and $\text{Pt}(\text{OH})_6\text{K}_2$, are obtained. That these salts correspond with the formulæ given to them and are not mere hydrates of PtO_3Na_2 or PtO_3K_2 , appears to be proved by the fact that they do not lose water at 100—110°, and that their aqueous solutions give with silver or thalious acetates, precipitates of the composition $\text{Pt}(\text{OH})_6\text{Ag}_2$ and $\text{Pt}(\text{OH})_6\text{Tl}_2$, which are also stable at 100°. Moreover, when water has been eliminated from the salts by heating them at a high temperature, they do not easily become rehydrated. The acid which they regenerate when treated with acetic acid always has the composition $\text{Pt}(\text{OH})_6\text{H}_2$.
W. A. D.

Mineralogical Chemistry.

Carbonaceous Substances accompanying the Caucasian Naphtha Deposits. K. W. CHARITSCHKOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 695—701).—In some regions of the Caucasus (Grosny and Tschatma in the Tiflis government), the naphtha is accompanied by coal in the form of layers, alternating regularly with the naphtha

strata. In composition, this coal closely resembles brown coal, from which it differs only in containing less water and in being slightly hygroscopic. The Grosny coal contains large proportions of salts and sulphur; that from Tschatma occurs in two modifications; one, brown with a high salt content, and the other black, resembling ordinary coal, but containing less sulphur, nitrogen, and moisture than this. The intimate connection between this coal and the naphtha suggests that the former is a product of the metamorphosis of the latter, of its hydrogenation by the slow action of sulphur and heat. This view is supported by the formation of hydrogen sulphide from sulphur and naphtha and by the occurrence of coal in the pipes used for conveying heated naphtha. Further, the possibility of the formation of coal from hydrocarbons has been shown by Höfer's recent discovery of pseudomorphs of anthracite after argentite; the formation of these pseudomorphs is expressed by the equation:

$$2\text{Ag}_2\text{S} + \text{CH}_4 = 4\text{Ag} + 2\text{H}_2\text{S} + \text{C}.$$

T. H. P.

Constitution, Origin, and Dehydration of Laterite. THOMAS H. HOLLAND (*Geol. Mag.*, 1903, 10, 59—69. Compare Abstr., 1899, ii, 565).—Laterite is not a ferruginous clay, but is essentially identical with bauxite, the alumina being present in the form of hydrated oxides. It is a product of superficial weathering in tropical climates, brought about, it is suggested, by the action of low organisms, possibly akin to the so-called nitrifying bacteria. Kaolin, on the other hand, is of deep-seated origin. The spontaneous loss of water experienced by laterite is accompanied by the development of a concretionary, and, in places, of a microcrystalline structure: this appears to correspond with a gradual exothermic change from gibbsite, $\text{AlO}(\text{OH}) \cdot \text{H}_2\text{O}$, to the more stable diasporite, $\text{AlO}(\text{OH})$, the "crystalline affinity" of the latter compound being greater than the chemical affinity of the former.

L. J. S.

Composition of Indian Laterite. H. WARTH and F. J. WARTH (*Geol. Mag.*, 1903, 10, 154—159; and *Chem. News*, 1903, 87, 256—258. Compare preceding abstract).—Twenty-three analyses are given of laterite from various localities in India. One of them corresponds with gibbsite (Abstr., 1902, ii, 328); four with the purer variety of bauxite known as wocheinite; eight with ferruginous bauxite (Fe_2O_3 , 13.75—56.01 per cent.); and the remainder, which are "low-level" detrital laterites, with bauxite largely mixed with quartz-sand and clay. In the "high level" laterites occurring *in situ* of the first three of these groups, the combined silica (present as clay) varies from 0.23 to 4.20 per cent., being often less in amount than the titanium dioxide (probably present as ilmenite), which reaches 6.61 per cent. in one sample of the wocheinite variety.

L. J. S.

[Blue Apatite] in the Tíree Marble. ANANDA K. COOMÁRA SWÁMY (*Q. J. Geol. Soc.*, 1903, 59, 91—103).—A description is given of the pink, grey, and white marbles which occur as lenticles in the gneiss near Balephetrish in Tíree. The minerals present in the marbles are: calcite, dolomite, pyroxene, amphibole, forsterite, scapolite, mica,

sphene, apatite, orthoclase, spinel, and serpentine. The apatite occurs as elongated grains of a bright sky-blue colour in coccolite-scapolite-sphene aggregates in the pink marble; analysis, by W. C. Hancock, gave :

| CaO. | P ₂ O ₅ . | Cl. | SiO ₂ . | H ₂ O (hygroscopic). | Total. | Sp. gr. |
|-------|---------------------------------|------|--------------------|---------------------------------|--------|---------|
| 53.92 | 39.55 | 1.85 | 1.5 | 3.16 | 99.98 | 3.20 |

This occurrence is very similar to that of blue apatite in Ceylon (Abstr., 1901, ii, 111, 171; 1902, ii, 567). L. J. S.

[Nephelite, Laumontite, Baryto-celestite, &c.] WILLIAM POLLARD (*Summary of Progress, Geol. Surv. United Kingdom for 1902, 1903, 56—61*).—The following mineral analyses are given: I, nephelite, from a boulder of nephelite-ægirite-syenite-pegmatite at Coulmore, Ross-shire (compare Abstr., 1903, ii, 378). II, a white alteration product of nephelite (?) from a vein east of Ault a Mhullin. III, laumontite, from the Baveno granite quarries, Italy. IV, baryto-celestite, from the Chipping Sodbury railway-cutting, Gloucestershire.

| | SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | CaO. | MgO. | K ₂ O. | Na ₂ O. | Li ₂ O. | CO ₂ . | SO ₃ . | H ₂ O at 105°. | H ₂ O above 105°. | Total. |
|------|--------------------|----------------------------------|----------------------------------|-------|------|-------------------|--------------------|--------------------|----------------------------------|-------------------|---------------------------|------------------------------|--------|
| I. | 44.87 | 32.00 | 1.53 | 0.47 | — | 6.72 | 14.00 | — | — | — | 0.11 | 0.87 | 100.57 |
| II. | 43.35 | 31.93 | 0.78 | 1.53 | 0.28 | 6.16 | 8.03 | 0.15 | 0.57 | 1.67 | 0.38 | 5.47 | 100.30 |
| III. | 51.35 | 22.14 | 0.67 | 12.35 | — | — | — | — | — | — | 13.65 | | 100.16 |
| IV. | BaO. | | SrO. | | CaO. | | SO ₃ . | | Fe ₂ O ₃ . | | Loss on ignition. | | Total. |
| | 24.48 | | 31.89 | | 1.22 | | 39.03 | | 1.26 | | 1.81 | | 99.69 |

In some basic, igneous rocks from Scotland, small amounts (0.01—0.06 per cent.) of chromium and vanadium were found. Analyses are also given of phosphatic nodules, clay, mottled dolomitic limestone, and of pumice separated from the volcanic dust which fell in Barbados on May 7—8, 1902. L. J. S.

Physiological Chemistry.

Action of Pilocarpine and Atropine on Embryos. TORALD SOLLMANN (*Amer. J. Physiol.*, 1904, 10, 352—361).—Small doses of pilocarpine hasten the development of echinoderm embryos; larger doses or prolonged action produces the opposite result. Small doses of atropine have no effect; larger doses hinder development. When both drugs are used, the depressant action always predominates, and the observed resultant is always below the mathematical average.

W. D. H.

Specific Gravity of Blood. EMIL P. BAUMANN (*Brit. Med. J.*, 1904, 473—474).—Hammerschlag's method is easily available for clinical purposes and yields trustworthy results, provided that the uniform excess, which Levy showed is associated with the use of a hydrometer, is obviated by having the instrument specially standardised.

W. D. H.

Effect of Altitude on the Blood. GEORGE T. KEMP (*Proc. Amer. Physiol. Soc.*, 1903, xxxii—xxxv; *Amer. J. Physiol.*, 10).—Examinations of the blood in several healthy people were made at Cripple Creek (9,400 feet) and Pike's Peak (14,200 feet), and compared with those made at Champaign (700 feet). Details of the rapid increase of red corpuscles are given; in the morning, the small usual rise was at great altitudes increased to 1,000,000 per c.m. Another marked effect is an enormous rise in the number of platelets; many are increased in size; small, red corpuscles are also numerous, and a few nucleated ones are seen. The leucocytes are unaffected. The daily fluctuations in hæmoglobin are very great, but generally, although not always, run with the variations in the number of the corpuscles. Specific gravity is no index of the number of red corpuscles.

W. D. H.

Is there Free Glycerol in Normal Blood? ANTOINE MOUNEYRAT (*Compt. rend. Soc. Biol.*, 1903, 55, 1438—1440, 1596—1598, 1599—1600).—Polemical against Nicloux, who answers this question in the affirmative (compare *Abstr.*, 1903, ii, 438, 560, 660).

W. D. H.

Oxidation of Dextrose in the Blood. LEOPOLD JOLLY (*Compt. rend.*, 1903, 137, 771—772).—Alcohol in minute quantities exists in the blood, and is believed to originate from sugar; the corpuscles are stated to effect the oxidation, and also to carry it further by converting some of the alcohol into acetic acid.

W. D. H.

Increase in the Glycolytic Power of the Blood after Ligation of Wirsung's Duct. RAPHAEL LÉPINE and BOULUD (*Compt. rend. Soc. Biol.*, 1903, 55, 1444—1445).—After the ligation of the pancreatic duct in dogs, and the administration of acidified water to excite secretion from that organ, the glycolytic power of the blood is increased.

W. D. H.

Amount of Proteids in Blood Plasma. JOHANN LEWINSKI (*Pflüger's Archiv*, 1903, 100, 611—633).—In human blood-plasma, the amount of serum-albumin is always greater than that of serum-globulin, the percentage of the former varying between 3·3 and 4·5, and of the latter between 2·4 and 3·8; fibrinogen varies between 0·27 and 0·48 per cent. During normal pregnancy, no noteworthy differences were seen; in puerperal eclampsia, the total proteid is somewhat lessened, and the fibrinogen increased. A large number of observations on the amount of the blood proteids in the lower animals are given. In all except the horse, serum-albumin is the most abundant proteid. The results of alternate periods of

feeding and inanition in dogs are inconstant, except that all show a slight rise in the amount of serum-globulin during inanition.

W. D. H.

Proteids of Blood-plasma in Experimental Infections. LEO LANGSTEIN and MARTIN MAYER (*Beitr. chem. Physiol. Path.*, 1903, 5, 69—82).—Under the influence of pneumococcus and streptococcus infection, there is a great increase in the fibrinogen of the blood plasma. It is not so marked in other infections which were tried. The increase of fibrin yield and globulin in inflammatory conditions in man has been noted previously by Halliburton and others. In normal rabbits, the proteid quotient (globulin:albumin) is 1:2. In almost all infections this rises and may reach 1:1. The total proteid is also usually increased.

W. D. H.

Changes in the Blood by Injection of Proteid. LEOPOLD MOLL (*Beitr. chem. Physiol. Path.*, 1903, 4, 578—589).—Rabbits and dogs were injected with a foreign proteid (horse-serum), as in experiments on immunity. The total proteid in their blood remained constant, but the globulin was increased, the increase being especially seen in the euglobulin fraction. Whether this is related to the development of the precipitin reaction is discussed, and in its favour it was found that, in the precipitate, the globulin of the immune serum alone participated. In this reaction, the proteid of the immune serum is the passive reagent; the precipitin it contains is the substance precipitated; precipitin and precipitate stand in relation to each other in the same way as fibrinogen and fibrin.

W. D. H.

Lipase of the Blood. CHARLES GARNIER (*Compt. rend. Soc. Biol.*, 1903, 55, 1423—1425, 1425—1427. Compare Abstr., 1903, ii, 560, 583, 660).—The lipasic power of human serum was tested in various diseases, infections, and poisonings. Such observations are stated to be of diagnostic value in certain cases, for instance, the power is increased in diabetes and lessened in latent gastric neoplasm. Return to the normal is favourable from the prognostic point of view.

W. D. H.

Action of Radium Emanations on Hæmoglobin and Red Corpuscles. VICTOR HENRI and ANDRÉ MAYER (*Compt. rend. Soc. Biol.*, 1903, 55, 1412—1414, 1414—1416).—The action of radium emanations on a solution of hæmoglobin is to transform it gradually into methæmoglobin. At the same time, the solubility of the substance diminishes. The action of the emanations on the red corpuscles is to modify their osmotic properties, so that they part with their pigment to isotonic solutions, and in relation to hypotonic solutions, they part with pigment and salts more than normal corpuscles do.

W. D. H.

Influence of Hæmorrhage on Proteid Katabolism. PHILIP B. HAWK and WILLIAM J. GIES (*Proc. Amer. Physiol. Soc.*, 1903, xxviii—xxix; *Amer. J. Physiol.*, 10).—Hæmorrhage in dogs does not

affect the fæces. The urine is entirely stopped for half an hour if the hæmorrhage amounts to 3 per cent. of the body weight, then follows a stage of diminished secretion and diminished specific gravity of the urine; 24 to 48 hours later, the reverse is seen. The nitrogen and sulphur show a slight temporary increase, the phosphorus a decrease. Repeated hæmorrhages produce cumulative katabolic effects.

W. D. H.

Influence of Hæmorrhage on Lymph. E. R. POSNER and WILLIAM J. GIES (*Proc. Amer. Physiol. Soc.*, 1903, xxxi—xxxii; *Amer. J. Physiol.*, 10).—After hæmorrhage in both well-fed and fasting dogs, the flow of lymph from the thoracic duct is diminished; the percentage of organic solids sometimes rises, sometimes falls, the ash remaining constant and equal to that of the blood. Sodium chloride injections produce as well-marked lymphagogue effects as in a normal animal.

W. D. H.

Uptake of Iron by the Human Placenta from the Maternal Blood. I. J. HOFBAUER (*Zeit. physiol. Chem.*, 1903, 40, 240—248).—The uptake of iron from the blood by the placenta is undoubted, and the power of splitting up the iron compounds resides in the chorionic cells.

W. D. H.

Blood Supply and Nutrition of the Pancreas. OTTO MAY (*J. Physiol.*, 1904, 30, 400—413).—The pancreas is well supplied with vaso-constrictor nerves. After injection of secretin, there is well marked vaso-dilatation, as shown by the plethysmographic method. This is secondary to secretion, and probably the result of the action of katabolic products on the vessels. No direct relation exists between rate of secretion and extent of blood supply in this organ. Secretion continues after cessation of the circulation.

W. D. H.

Metabolism Experiments. WILLIAM J. GIES (*Proc. Amer. Physiol. Soc.*, 1903, xxii—xxiii; *Amer. J. Physiol.*, 10).—Improved methods for performing metabolism experiments on dogs are described, and also a new form of cage to allow of easy quantitative collection of excreta. Bone ash is a desirable addition to the diet; it increases the bulk of the fæces, and ensures frequent and regular discharges; they also dry quickly and do not adhere to the cage. Charcoal is used to mark off periods.

W. D. H.

Metabolism following a small increase in Proteid Ingested. PHILIP B. HAWK and JOSEPH S. CHAMBERLAIN (*Amer. J. Physiol.*, 1904, 10, 269—289).—The experiments were made on man. The nitrogen excretion, measured by three hour periods, showed two maxima daily; it rises from the morning meal to mid-day, then falls, and rises again about the time of the evening meal. Measured by shorter periods, a third rise occurs between the other two. In general terms, the sulphates run a similar course. The rises in phosphate excretion occur later. After taking a small amount of extra proteid food, the time required to reach the maximum is prolonged, and the prolongation

is greater when the increase of proteid is greater. Alterations were also noted in the course of the excretion of the salts. The normal was not regained until four days later. W. D. H.

Nitrogenous Metabolism after Splenectomy. LAFAYETTE B. MENDEL and ROBERT B. GIBSON (*Proc. Amer. Physiol. Soc.*, 1903, xxix—xxx; *Amer. J. Physiol.*, 10).—In a case of splenectomy in man, the character of the curves of post prandial excretion of uric acid and other nitrogenous constituents of urine was normal; chlorides were retained during febrile conditions; the organism's capacity to form uric acid from purine substances in the food was undiminished, and there is a relatively large output of endogenous uric acid; the excretion of urobilin was marked at times. Possibly the two latter conditions were due to impaired hepatic conditions. W. D. H.

Origin of Sulphur-containing Products of Metabolism in the Animal Organism. JULIUS WOHLGEMUTH (*Zeit. physiol. Chem.*, 1903, 40, 81—100).—In the rabbit, cystin causes an increase in the urinary sulphates and in the non-oxidised sulphur. In the normal animal, the ratio of neutral sulphur to oxidised sulphur is 1 : 4; after dosing with cystin it is 1 : 2. Sulphites are also present. If cystin is given by the mouth, the sulphur of the bile is increased, cystin being converted into taurine. W. D. H.

Coefficients of Digestibility and Availability of Foods. WILBUR O. ATWATER (*Proc. Amer. Physiol. Soc.*, 1903, xxx—xxxi; *Amer. J. Physiol.*, 10).—The coefficient of digestibility would be found by subtracting the undigested residue from the food; the coefficient of availability is found by subtracting the total excreta from the total food. Some hundreds of experiments on man have enabled data of such coefficients to be recorded, and the average shows the coefficient of availability for proteid to be 91.1, for fat 94.8, and for carbohydrate 96.8 per cent. In vegetable diet, the availability of the proteid is less. W. D. H.

Solubility in Gastric Juice of the Nitrogenous Constituents of Sheep's Fæces. CARL BEGER (*Zeit. physiol. Chem.*, 1903, 40, 176—181).—Comparing the fresh with the dried material, the amount of the nitrogenous substances indigestible by pepsin-hydrochloric acid is lower in the former. The solubility of the proteid is 6.3 per cent. greater in the fresh material. Differences on different kinds of diet are given. W. D. H.

Peptic and Tryptic Digestion of Proteids. D. LAWROFF (*Zeit. physiol. Chem.*, 1903, 40, 165—166).—Polemical against Salaskin and Kowalewsky (*Abstr.*, 1903, ii, 559). In 1871, Lubavin described the occurrence of leucine and tyrosine among the products of the peptic digestion of casein. In 1901, the author showed that after 2 months' peptic digestion with commercial pepsin, or the natural gastric juice, the products obtained from casein and gelatin contained substances not precipitable by phosphotungstic acid. W. D. H.

Inversion of Sucrose in the Stomach. GRAHAM LUSK (*Proc. Amer. Physiol. Soc.*, 1903, xxi—xxii; *Amer. J. Physiol.*, 10).—Further experiments are given which uphold the author's previous conclusion that the inversion of sucrose which occurs in the stomach is entirely due to the acid. No evidence of an enzyme was found. W. D. H.

Acid Formation in the Stomach. LEO SCHWARZ (*Beitr. chem. Physiol. Path.*, 1903, 5, 56—68).—The secretion of acid in the stomach is accompanied by a decrease in the acidity of the urine due to the increase of carbonate there. In chlorine hunger in dogs, the administration of sodium chloride or bromide (but not iodide) stimulates the gastric mucous membrane, and at the same time the effect of increased carbonates is seen in the urine. In normal animals, these salts do not produce this effect. W. D. H.

Plasteinogen. H. BAYER (*Beitr. chem. Physiol. Path.*, 1903, 4, 554—562).—Plastein is the name given by Sawjaloff (*Abstr.*, 1901, ii, 403) to the precipitate formed on the addition of rennin to albumose solutions. Its parent substance may be named plasteinogen; this is neither proto- nor hetero-albumose, but a later product of digestion; the non-proteid products which occur last in the proteolytic process yield no plastein. Plasteinogen is soluble in 80 per cent. alcohol and acetone; it is a proteid of simple composition containing the tyrosine, cystin, and probably also the carbohydrate and indole nuclei. Analysis of plastein does not confirm the hypothesis that this substance is regenerated proteid. W. D. H.

Nutritive Value of Alcohol. RUDOLF ROSEMAN (*Pflüger's Archiv*, 1903, 100, 348—366. Compare *Abstr.*, 1901, ii, 668).—A further contribution to a much discussed question, which upholds the author's previously expressed view that alcohol within certain limits is of nutritional value. W. D. H.

Formation of Sugar from Leucine. JOHN T. HALSEY (*Amer. J. Physiol.*, 1904, 10, 229—235).—Although the possibility that the leucine complex as it exists in proteid may be concerned in sugar formation still remains, the experiments recorded led the authors to believe that pure leucine administered to phloridzinised dogs is not changed into sugar. W. D. H.

Coagulative Action of Autolytic Organ Extracts on Milk and on Albumose Solutions. A. NÜRNBERG (*Beitr. chem. Physiol. Path.*, 1903, 4, 543—553).—Extracts of organs subjected to aseptic autolysis have a coagulative action on solutions of albumose; the liver gives the most marked result; then follow in order stomach, lung, pancreas, intestine, kidney, brain, and muscle. With regard to milk, the order is different; here the pancreas comes first, especially with fresh extracts; these are even more rapid in their rennet-like action than fresh extracts of the stomach. On albumose solutions, stomach extracts act best if faintly acid; the influence of reaction is not so marked in the case of

other organs, but there are individual differences ; the best results were obtained with organs from the pig, after 16 hours' autolysis.

W. D. H.

End-products of Auto-digestion of Animal Glands. PHOEBUS A. LEVENE (*Proc. Amer. Physiol. Soc.*, 1903, xxxviii ; *Amer. J. Physiol.*, 10).—The communication relates only to the amino-acids obtained on the auto-digestion of liver and pancreas, the former in 0.2 per cent. solution of acetic acid, the latter in 0.5 per cent. solution of sodium carbonate. Alanine, aminovaleric acid, leucine, glutamic and aspartic acids, tyrosine, and phenylalanine were identified. The presence of pyrrolidine-2-carboxylic acid could not be established with certainty.

W. D. H.

End-products of Tryptic Digestion of Gelatin. PHOEBUS A. LEVENE (*Proc. Amer. Physiol. Soc.*, 1903, xxxix ; *Amer. J. Physiol.*, 10).—Gelatin contains more glycine than gelatin ; gelatin peptone contains less than gelatin. The crystalline products of digestion were therefore studied. Those found were glycine in very large quantities, leucine, glutamic acid, in smaller quantities, phenylalanine, and a substance having the composition of inactive pyrrolidinecarboxylic acid ; the copper salt which was analysed differs in appearance from that of the 2-acid.

W. D. H.

The Liver. LUDOLPH BRAUER (*Zeit. physiol. Chem.*, 1903, 40, 182—214).—Methylene-blue, which is employed therapeutically for cholelithic affections, is excreted by the bile in much larger amount than by the urine. In normal bile, and in the bile of alimentary glycosuria, and of phloridzin diabetes, sugar is absent in the bile or only traces occur. In pancreatic diabetes, the bile contains 0.8 per cent. or less of sugar. Ethyl and amyl alcohols pass easily into the bile and produce irritation of the liver parenchyma ; the bile in these circumstances is usually albuminous. There is also irritation of the epithelium of the bile ducts, and appearances similar to urinary casts are seen in the bile.

W. D. H.

An Oxidising and Reducing Ferment in the Liver. J. E. ABELOUS and JULES ALOY (*Compt. rend.*, 1903, 137, 885—887).—From experiments conducted with aqueous extracts of horses' liver and alkaline nitrates and salicylic acid, the conclusion is drawn that the ferment which produces reduction in one case, and oxidation in the other, is one and the same substance.

W. D. H.

The Sugar-forming Ferment of the Liver. L. BORCHARDT (*Pflüger's Archiv*, 1903, 100, 259—297).—The sugar obtained from the liver after death is sometimes almost exclusively dextrose, at other times this is mixed with maltose and isomaltose. Like the similar ferment in the blood, the action of the liver ferment on glycogen leads to the formation of dextrans as intermediate products. Achroodextrin is readily obtained. The same ferment action can be obtained with

liver previously coagulated by alcohol. The results are mainly confirmatory of those previously described by Bial, Shore, Pavy, Tebb, and others. W. D. H.

Autolysis. JULIUS ARNHEIM (*Zeit. physiol. Chem.*, 1903, 40, 234—239).—The addition of gelatin to a liver allowed to digest itself increases the formation of peptone and amino-acids. Carbohydrates also further the action. Certain neutral salts investigated have no effect. W. D. H.

Glycolysis. JULIUS ARNHEIM and ADOLF ROSENBAUM (*Zeit. physiol. Chem.*, 1903, 40, 220—233).—All the tissues investigated have a glycolytic action; the addition of pancreas to other tissues increases this action. W. D. H.

Absorption of Iron in the Rabbit. S. TARTAKOWSKY (*Pflüger's Archiv*, 1903, 100, 586—610).—This is a microchemical study, and the conclusion is reached that iron given as a drug is absorbed in the same way and accumulates in the same organs as the ordinary iron of the nutriment. W. D. H.

The Passage of Different Foods from the Stomach. W. B. CANNON (*Proc. Amer. Physiol. Soc.*, 1903, xvii—xviii; *Amer. J. Physiol.*, 10).—Röntgen ray shadows cast by various foods mixed with bismuth subnitrate afford a method of estimating the relative amount of food in the intestines. In the cat, the discharge of proteids from the stomach is delayed as compared with carbohydrate; this is due to the absence of free acid at first, but if the proteid be rendered acid beforehand, and the carbohydrate alkaline this is reversed. Acid in the stomach is the stimulus for the opening of the pyloric orifice, and in the intestine for its closure. W. D. H.

Influence of Tannin and Morphine on the Absorption of Sodium Chloride in the Small Intestine. BIBERFELD (*Pflüger's Archiv*, 1903, 100, 252—258).—Tannin of 1 per cent. concentration reduces absorption from within an intestinal loop to one-third; with 0.1 per cent. concentration it is hastened, whilst with a concentration of 0.04 per cent. there is no effect. Morphine given as 0.1 per cent. solution of aqueous extract of opium, or as small doses of the hydrochloride, hastens absorption markedly. W. D. H.

Influence of Castration. ROBERT BREUER and RUDOLF (FREIHERR) VON SEILLER (*Chem. Centr.*, 1903, ii, 1340; from *Arch. exp. Path. Pharm.*, 50, 169—198. HUGO LÜTHJI, *ibid.*, 1341, from *ibid.*, 268—272).—Castration in young female dogs has no ill effects; the body-weight is maintained, but the hæmoglobin and red corpuscles of the blood diminish in parallel lines. In either sex, the operation has no influence on the metabolism of proteid, fat, phosphoric acid, or calcium. W. D. H.

Osmotic Properties of Muscle. W. M. FLETCHER (*J. Physiol.*, 1904, 30, 414—438).—A detailed account of work previously abstracted (*Abstr.*, 1903, ii, 90). W. D. H.

Effects of Salts on the Tonicity of Skeletal Muscle. WILLIAM D. ZOETHOUT (*Amer. J. Physiol.*, 1904, 10, 211—221).—The salts of potassium, caesium, ammonium, and rubidium increase the tonicity of skeletal muscles. The iodide, bromide, and sulphate have a greater effect than the chloride. The chlorides of sodium, lithium, and especially calcium, strontium, and magnesium abolish this effect. Certain salts (iodide, bromide, sulphate) of sodium may increase the tone, but this action is slight compared with their power to cause rhythmical action; the action of lithium salts is still less. Barium chloride antagonises the action of potassium chloride in preventing tonicity, and potassium chloride antagonises the action of barium chloride in preventing rhythmical action.

W. D. H.

Effects of Ringer's Fluid on Plain Muscle. RAGHAVENDRA Row (*J. Physiol.*, 1904, 30, 461—475. Compare Abstr., 1903, ii, 498).—The influence of Ringer's fluid on the plain muscle of the frog's stomach is to maintain its irritability, and keep up rhythmical action for hours, acting, in fact, as it does on the heart. The presence or absence of potassium chloride on the fluid is immaterial. Sodium chloride alone leads to gradual diminution and abolition of the movements; here again is a resemblance to heart muscle. An initial augmentation seen in plain muscle with this salt is, however, absent in the case of the heart. Calcium chloride acts on plain exactly as it does on skeletal muscle.

W. D. H.

Production of Contact Irritability without the Precipitation of Calcium Salts. WILLIAM D. ZOETHOUT (*Amer. J. Physiol.*, 1904, 10, 324—334).—The chlorides of potassium, caesium, ammonium, rubidium, and perhaps barium aid the development of, although they do not produce, contact irritability. The chlorides of sodium, lithium, magnesium, and calcium inhibit it. In the normal muscle, only those salts of sodium that precipitate calcium can produce it, but if caesium or rubidium chloride is introduced into the muscle simultaneously with the acetate, succinate, or nitrate of sodium, contact irritability is established.

W. D. H.

Biochemical Synthesis. SAMUEL B. SCHRYVER (*Proc. Physiol. Soc.*, 1904, xlv—xlvi; *J. Physiol.*, 30).—Aldehydes act on ethyl malonate, producing a series of condensation products (Claissen and Komnenos). Knoevenagel showed that this will occur even at low temperatures in the presence of piperidine and other bases acting catalytically. The present paper seeks an answer to the question whether such a reaction plays any part in the carbohydrate metabolism in the body, but with all the experiments recorded with bases from the organs, negative results were obtained.

W. D. H.

Albumins from the White of Rooks' Eggs. WLADIMIR W. WORMS (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 835—844).—The white of rooks' (*Corvus frugilegus*) eggs contains two white substances: (1) one insoluble in semi-saturated ammonium sulphate solution; and (2) the

other, present in larger quantity, readily soluble in this solution. The latter consists of three albumins, named by the author *corvin*, *corvinin*, and *corvinidin*, possessing different compositions.

T. H. P.

Rôle of Leucocytes in Fibrin Formation. E. MAUREL (*Compt. rend. Soc. Biol.*, 1903, 155, 1492—1494).—Observations which lead the author to doubt whether the leucocytes have anything to do with the formation of fibrin.

W. D. H.

Enzyme of the Thymus and Suprarenal. WALTER JONES (*Proc. Amer. Physiol. Soc.*, 1903, xxiv—xxv; *Amer. J. Physiol.*, 10).—Autodigestion of the thymus and of the nucleo-proteid of the thymus led to the formation of phosphoric acid and xanthine bases, of which xanthine itself and hypoxanthine were separated. The hydrolytic products of thymonucleic acid are adenine and guanine. The same results were obtained with the suprarenal.

W. D. H.

Mineral Constituents of Cow's Milk and their Variations in the Course of a Lactation Period. AUGUST TRUNZ (*Zeit. physiol. Chem.*, 1903, 40, 263—310. Compare Abstr., 1903, ii, 742).—A continuation of the author's work, in which numerous analyses of the inorganic constituents are presented in tabular form.

W. D. H.

Local Application of Saline Purgatives to the Peritoneal Surface of the Intestine. JOHN B. MACCALLUM (*Amer. J. Physiol.*, 1904, 10, 259—268. Compare Abstr., 1903, ii, 742).—Small quantities of saline purgatives (barium chloride, sodium citrate, and sulphate) applied to the peritoneal surface of the intestine produce increased peristalsis. This may be inhibited by the local application of calcium or magnesium chloride. The purgatives in question cause increased secretion whether given subcutaneously, intravenously, or applied locally; this can be inhibited in the same way.

W. D. H.

The Physical Factors in Urine Formation. TORALD SOLLMANN and R. A. HATCHER (*Proc. Amer. Physiol. Soc.*, 1903, xxv—xxvii; *Amer. J. Physiol.*, 10).—In an excised and perfused kidney, the amount of chloride in the perfusing fluid and the ureter filtrate is the same. The kidney volume and the flow from vein and ureter run parallel to the injection pressure. Compression of the vein stops the ureter flow. Numerous other circumstances, including the admixture of various drugs, &c., to the perfusing fluid cause variations which are described.

W. D. H.

Effect of Diuretics with a Diet Poor in Salts. H. D. HASKINS (*Amer. J. Physiol.*, 1904, 10, 362—363).—Sollmann showed that in rabbits diuretics with a diet poor in salts produce an increase of urinary chlorides, but this is not the case in dogs, whose kidneys are more resistant. The present experiments show that the human kidney belongs to the resistant class.

W. D. H.

Elimination of Sugar and Compounds of Glycuronic Acid under the Influence of Traumatism, and Injections of Sugar into the Blood. CADÉAC and MAIGNON (*Compt. rend. Soc. Biol.*, 1903, 55, 1464—1466. Compare Abstr., 1903, ii, 310, 675).—Traumatism leads to an elimination in the urine of glycuronic acid and often of sugar. The sugar originates in the injured tissues. Injection of sugar into the blood stream insufficient in amount to cause glycosuria leads to the appearance of glycuronic acid in the urine; if this limit is exceeded, sugar appears as well. W. D. H.

The Nitrogen Excretion in a Case of Phosphorus Poisoning. RUDOLF VON JAKSCH (*Zeit. physiol. Chem.*, 1903, 40, 123—147).—In the case recorded, the products of nitrogenous metabolism (ammonia, uric acid, amino-acids, and especially urea) were increased in the urine. The urea estimations were made by the Schöndorff and Mörner-Sjoqvist methods, which gave closely accordant results. W. D. H.

Urea of Human Urine. WM. OVID MOOR (*Zeit. physiol. Chem.*, 1903, 40, 162—164. Compare Abstr., 1903, ii, 343).—Polemical against Erben (Abstr., 1903, ii, 581). The author maintains that the urea of the urine amounts to only one-half or even less of what is usually stated to be the case.

WILLIAM J. GIES (*J. Amer. Chem. Soc.*, 1903, 25, 1295) holds that the substance Moor isolated from urine and termed *ureine* is a mere mixture of different organic and (mainly) inorganic constituents of urine. W. D. H.

Influence of Diet on Uric Acid Excretion. PAUL PFEIL (*Zeit. physiol. Chem.*, 1903, 40, 1—24).—With diet free from meat in healthy men, the excretion curve of uric acid shows individual differences, but is nearly a straight line with a slight rise in the morning. If the diet is completely free from nitrogen, the same values are obtained. With a mixed diet containing abundance of meat (320 to 350 grams per diem), there is a great rise which reaches its summit four hours after the meat is taken; the actual amount excreted shows individual differences. W. D. H.

Influence of Diet on Uric Acid Excretion in Uric Acid Arthritis. FRANZ SOETBEER (*Zeit. physiol. Chem.*, 1903, 40, 25—54). **Metabolism in Gout.** FRANZ SOETBEER (*ibid.*, 55—61. Compare Abstr., 1902, ii, 417).—In five patients, the uric acid in the urine was estimated at three hour intervals; on a diet free from meat, there are only small differences from the normal curve (see preceding abstract); the morning rise is generally absent, but unexpected sudden rises occur during the day. On a mixed diet with excess of meat, in acute gout the large rise in the curve is absent. In chronic gout also, where the kidneys are normal, irregularities in the curve are noted, and in one case the rise after intake of meat was completely absent.

In a case of gout, between the attacks, on a mixed diet, there was in two days an excretion of potassium less by 3.5 grams than in normal

persons. The excretion of ammonia and of uric acid was very low, but the acidity of the urine was increased. W. D. H.

Increase of Uric Acid Excretion in Cats after Administration of that Substance by the Mouth. ARTHUR KANGER (*Pflüger's Archiv*, 1903, 100, 428—441).—There is an increase in the uric acid excreted in the urine of the cat after that substance is given by the mouth. The quantity excreted is, however, much less than that given. Hopkins' method of estimation was used. W. D. H.

Acid Dyscrasia. ALEXANDRE DESGREZ and J. ADLER (*Compt. rend.*, 1903, 137, 818—819).—The subcutaneous injection of dilute solutions of hydrochloric acid in guinea pigs lessens the amount of hippuric acid excreted by nearly one-half, owing to impairment of the synthetic power of the living cells. W. D. H.

The Fate of Cystin in the Body. L. BLUM (*Beitr. chem. Physiol. Path.*, 1903, 5, 1—14).—Cystinuria is due to an abnormal form of proteid metabolism; it does not occur when cystin is given by the mouth. When cystin is injected intravenously, it is only in part utilisable, the rest leaving by the urine. Experiments, in which the injection was made into a mesenteric vein, and others in which the minced liver was employed, indicate the liver as the main seat of the decomposition into urea which occurs. The kidneys and blood play no part in this. Further details are promised regarding the organic sulphur compounds which originate from cystin. W. D. H.

Nature of Urinary Indican. LOUIS MAILLARD (*Compt. rend. Soc. Biol.*, 1903, 55, 1332—1334, 1334—1335).—Polemical against Monfet (this vol., ii, 63, 102). W. D. H.

Precursors of Urinary Indican. FRANK P. UNDERHILL (*Proc. Amer. Physiol. Soc.*, 1903, xxvii; *Amer. J. Physiol.*, 10).—Indole from intestinal putrefaction is doubtless the main precursor of indican in the urine. Tryptophan may be a precursor of indole. Tryptophan is scatole-aminoacetic acid, and the Adamkiewicz reaction of proteids is due to tryptophan (Hopkins and Cole). Among proteids, some (notably gelatin) fail to give the test. Feeding with gelatin as the sole nitrogenous article in the diet, causes a marked decrease of urinary indican. W. D. H.

Indoxyluria. FRITZ ROSENFELD (*Beitr. chem. Physiol. Path.*, 1903, 5, 82—94, and *Chem. Centr.*, 1903, ii, 1464; from *Verh. Vers. Deut. Naturf. Aerzte*, 1902, ii, 61—64).—In rabbits receiving a small but adequate amount of suitable food, no indoxyl appears in the urine; if this is diminished, indoxyl appears. The same result follows injection of phloridzin. Here indoxyl does not originate from intestinal putrefaction, but from the breakdown of tissues. Tryptophan appears to be an intermediate substance in its formation. W. D. H.

Ehrlich's Diazo-reaction. LOUIS MAILLARD (*Compt. rend. Soc. Biol.*, 1903, 55, 1419—1421, 1421—1423).—Monfet (this vol., ii, 63) attributes this reaction to urinary indican, and in confirmation states that the reaction is given by certain indigo-yielding plants. The plant reactions described are spoken of as "banal," but, such as they are, are produced by the yellow pigments of the leaves which belong to the tannin group. Conjugated indoxyl as it occurs in urine plays no part in the reaction. W. D. H.

Neutral Sulphur and Ehrlich's Diazo-reaction. L. MONFET (*Compt. rend. Soc. Biol.*, 1903, 55, 1503—1505; LOUIS MAILLARD, *ibid.*, 1508—1509).—The diazo-reaction is still regarded by the first author, in spite of criticisms, as due to excess of conjugated aromatic sulphates. He admits that many of his conclusions have been hasty. On a flesh diet, and during diarrhoea, the reaction is intense; after a saline purge or vegetable diet, it lessens. The second paper contains more criticisms. W. D. H.

Ether-Anæsthesia. PHILIP B. HAWK (*Proc. Amer. Physiol. Soc.*, 1903, xxxvii—xxxviii; *Amer. J. Physiol.*, 10).—In ether anæsthesia, the urinary flow is diminished; afterwards there is slight diuresis with a small rise in total nitrogen and a large rise in chlorine excretion. Glycosuria always occurs unless the animal (dog) is fasting. There is an increase in both the red and white blood corpuscles. W. D. H.

The Relation of Blood Pressure and Pulse Pressure to Urinary Secretion in a Case of Physiological Albuminuria. JOSEPH ERLANGER and DONALD R. HOOKER (*Proc. Amer. Physiol. Soc.*, 1903, xvi; *Amer. J. Physiol.*, 10).—Posture, and hence pulse pressure, influences the composition of urine. The amounts of chlorides (especially) of total nitrogen and phosphates is increased by the recumbent position. In a case of so-called "physiological albuminuria," an increase of pulse pressure (measured by a new sphygmomanometer) accompanied an increase in the amount of urine, and a decrease in the albumin. W. D. H.

Variations in the Permeability of the Kidney for Sodium Chloride in the Course of Bright's Disease. WIDAL and ADOLPHE JAVAL (*Compt. rend. Soc. Biol.*, 1903, 55, 1532—1535, 1639—1642).—In Bright's disease, the impermeability of the kidney for sodium chloride (which is believed by the authors to be the main cause of albuminuria and œdema) is never absolute, but varies a good deal in the course of the malady, as is shown by the observations recorded. No such impermeability exists for urea. W. D. H.

The Urine in Beri-Beri. HERBERT E. DURHAM (*Brit. Med. J.*, 1904, i, 480—482).—Metabolism in this disease is much diminished. Urea, phosphoric acid, and sulphuric acid are much reduced in the urine. It should, however, be noted that Tamils, even on liberal diet, excrete less of these substances than Europeans, although their uric

acid output is high. In beri-beri, the purine substances show nothing of interest, and the conjugated sulphuric acid and neutral sulphur are not proportionately diminished. W. D. H.

Lævulose Diabetes. WILHELM SCHLESINGER (*Chem. Centr.*, 1903, ii, 1464—1465; from *Arch. exp. Path. Pharm.*, 50, 273—293).—In a case of rickets in a girl, lævulose free from dextrose appeared in the urine. On a mixed diet, 1·5 grams were excreted daily; on cessation of food, it disappeared. Starch and dextrose had no effect. If lævulose was given, 12·5 per cent. of it was excreted unchanged. One hundred grams of sucrose were given, and 11 of lævulose excreted. Inulin had no effect. Phloridzin injection led to the appearance of dextrose instead. Lævulose was looked for in 15 other cases of diabetes with negative result. In two cases, there was excretion of sucrose after abundant carbohydrate food. W. D. H.

Tuberculins. BÉRANECK (*Compt. rend.*, 1903, 137, 889—891).—The toxins produced in tuberculosis are numerous, and vary with the reaction of the medium in which the bacillus is grown. In the course of a cultivation, neutral and alkaline media become acid. The different toxins produce different symptoms, and in their therapeutic action it is necessary to take this fact into account. W. D. H.

Intravenous Injection of Sodium Hydrogen Carbonate after Severe Hæmorrhage. PERCY M. DAWSON (*Proc. Amer. Physiol. Soc.*, 1903, xxxv—xxxvi; *Amer. J. Physiol.*, 10).—Sodium hydrogen carbonate injection restores cardiac action better than solutions of sodium chloride. The beneficial action persists longer with a mixture of 0·8 per cent. of sodium hydrogen carbonate and 0·25 per cent. of sodium chloride. W. D. H.

Action of Bismuth. GOTTHOLD FUCHS (*Chem. Centr.*, 1903, ii, 1464; from *Verh. Vers. Deut. Naturf. Aerzte*, 1902, ii, 90—94).—The secretion of mucus is no mere mechanical effect of bismuth crystals, but specific. The beneficial action of bismuth salts is due to reduction to a lower oxide which passes into the granulation tissue. Bismuthose, a compound with proteid, is specially recommended. W. D. H.

Intravascular Injection of Salts and Nucleo-proteid. J. A. MACWILLIAM, A. H. MACKIE, and CHARLES MURRAY (*J. Physiol.*, 1904, 30, 381—399).—Small amounts of sodium carbonate and magnesium sulphate induce disturbances of respiration and circulation, and so should not be used as anti-coagulants in blood-pressure work. Sodium sulphate is a better salt to use for such purposes, and best of all are sodium citrate (1 per cent.) and sodium oxalate (0·2 per cent.), which produces no disturbance. A 1 per cent. solution of sodium carbonate is usually employed to dissolve nucleo-proteid in experiments on intravascular coagulation; this solution alone, however, often causes arrest of respiration and muscular twitchings. The exophthalmus that occurs in fatal injections of nucleo-proteid is due to hæmorrhage in the orbit.

Nucleo-proteid causes no coagulation in blood shut up in an artery or vein. It is apparently in the capillary area that the conditions for this result are present.

When the circulation is shut off from the lower half of the body (below the diaphragm), nucleo-proteid injection readily causes coagulation. The "negative phase" is not seen in these circumstances or in the blood shut up within a large vessel. This phase is possibly due to the genesis of anti-substances in the abdominal viscera.

W. D. H.

The Fate of Monoamino-acids in the Body after Intravascular Injection. KARL STOLTE (*Beitr. chem. Physiol. Path.*, 1903, 5, 15—26).—Some of the amino-acids (tyrosine and phenylalanine) cannot with certainty be found to increase the urea in the urine after intravenous injection in rabbits. Others (alanine, aspartic acid, glutamic acid, cystin) increase the urea nitrogen and also that of the monoamino-acid fraction. In other cases, again, they are so quickly broken up that there is only an increase of urea. Leucine and glycine belong to the last group.

W. D. H.

Immunisation of Rabbits against the Hæmolytic Action of Sodium Taurocholate. E. RIST and L. RIBADEAU-DUMAS (*Compt. rend. Soc. Biol.*, 1903, 55, 1519—1521, 1521—1522).—By the gradual immunisation of the rabbit with the bile salt, the resistance of its red corpuscles towards the hæmolytic action of that reagent is increased. There is also increased activity of the blood-forming tissues.

W. D. H.

Physiological Action of Cyclic isoOximes, Ketones, Imines, and Oximines of the Hydroaromatic Series. CARL JACOB, HARNO HAYASTIE, and SZUBINSKI (*Chem. Centr.*, 1903, ii, 1343, from *Arch. exp. Path. Pharm.*, 50, 199—246).—The following were the substances investigated: cyclic ketones (pentanone, hexanone, camphor, &c.), cyclic imines (piperidine, &c.), cyclic isooximes (oxypiperidine, &c.), alkyl substitution products of cyclic isooximes, and cyclic oximes. The main symptoms are convulsions, central paralysis, and effects on motor nerve-endings.

W. D. H.

Actions of Adrenaline [Epinephrine]. MAURICE LOEPER (*Compt. rend. Soc. Biol.*, 1903, 55, 1452—1453, 1453—1455).—Adrenaline produces hæmolysis, stimulates the activity of tissues where new blood corpuscles are formed, after a time leads to atheroma, and punctiform hæmorrhages in the suprarenal gland. Bad effects are avoided if the substance is injected subcutaneously.

W. D. H.

Effect of Adrenaline [Epinephrine] on Pulmonary and other Vessels. T. GREGOR BRODIE and WALTER E. DIXON (*J. Physiol.*, 1904, 30, 476—502).—The rate of flow perfused at constant pressure through the vessels was used to determine the calibre of the arterioles. Stimulation of vaso-constrictor nerves of limbs or intestines gives a positive result more than two hours after death. Adrenaline,

pilocarpine, muscarine, and barium chloride all cause constriction. No evidence was found of any vaso-motor supply to the pulmonary arterioles. Here, of the drugs mentioned, barium chloride alone causes constriction; the others act as dilators; the systemic vessels behave like the pulmonary when constrictor nerve-endings are paralysed by apocodeine or curare. The general conclusion drawn is that barium chloride acts on muscle fibres, whilst the other three substances cause constriction by acting on nerve-endings.

W. D. H.

Relation between Solution Tension, Atomic Volume, and Physiological Action of the Elements. ALBERT P. MATHEWS (*Amer. J. Physiol.*, 1904, 10, 290—323).—The poisonous action of salts as tested on *Fundulus* eggs varies inversely with the sum of the solution tensions of both ions, that is, with the decomposition tension of the salt. There is an inverse relationship between atomic volume and poisonous action. Numerous exceptions to these rules are noted.

W. D. H.

Toxicity of Tetrphosphorus Trisulphide. A. E. THAYER and CHARLES G. L. WOLF (*J. Medical Research, Boston, U.S.A.*, 1903, 9, 191—216).—Tetrphosphorus trisulphide (P_4S_3), a substance largely employed in various manufactures, may be regarded as non-toxic in ordinary circumstances. Air which has been passed through it has no effect on rabbits. Given by the mouth in dogs, it acts as a mild local irritant of the small intestine, and to a less degree of the stomach. After prolonged treatment with small doses, or shorter treatment with large doses, it acts destructively on white blood corpuscles and the epithelial cells of renal cortex, liver, pancreas, and cardiac muscle in the order named; but the effect is not marked, and recovery is rapid on cessation of administering the material. Hæmolytic, jaundice, and the appearance of albumin, sugar, leucine, and tyrosine in the urine were never observed.

W. D. H.

Action of Radium on Simple Animals. E. G. WILLCOCK (*J. Physiol.*, 1904, 30, 449—454).—The lethal action of radium emanations varies with different species of animals. *Hydra viridis*, *Opalina*, and others show no sign of injury after 24 hours' exposure, whilst *Hydra fusca* and *Actinosphaerium* begin to disintegrate in a few hours.

W. D. H.

Toxicity of Hydroxyl Derivatives of Benzene. ALLYRE CHASSEVANT and CHARLES GARNIER (*Compt. rend. Soc. Biol.*, 1903, 55, 1584—1586).—Experiments were conducted with benzene, the mono-substitution derivative, phenol, disubstitution derivatives (catechol, resorcin, quinol), and the trisubstitution products (pyrogallol and phloroglucinol). The effects produced are convulsions and hypothermia; the toxicity increases in the order named, except in the case of the trisubstitution derivatives, the toxicity of which is only a little greater than that of benzene itself.

W. D. H.

Antagonism between Alkaloids and Salts. MARTIN H. FISCHER (*Amer. J. Physiol.*, 1904, 10, 345—351).—The experiments were limited to strychnine and the chlorides of calcium, barium, and magnesium, and sodium citrate. No antagonising action on animals was observable.
W. D. H.

Minimal Fatal Doses of Sparteine Sulphate. E. MAUREL (*Compt. rend. Soc. Biol.*, 1903, 55, 1339—1342).—The minimal lethal dose of sparteine sulphate is, per kilo. of body-weight, 0.15 gram for the conger and frog, 0.10 gram for the pigeon and rabbit.
W. D. H.

Toxicity of Sparteine Sulphate. E. MAUREL (*Compt. rend. Soc. Biol.*, 1903, 55, 1427—1428).—Sparteine sulphate is not a cardiac poison. It kills by arrest of the respiration, due to its action both on nerves and muscles. The favourable action of therapeutic doses in the circulation is due to its action on the peripheral vessels, not on the heart.
W. D. H.

Ricin. T. B. OSBORNE and LAFAYETTE B. MENDEL (*Proc. Amer. Physiol. Soc.*, 1903, xxxvi—xxxvii; *Amer. J. Physiol.*, 10).—The proteids of the castor oil bean are an albumin, a globulin, and a proteose. The two latter are the most abundant, and are not toxic. The toxicity of the purified albumin is very great, 0.002 mg. per kilo. of body-weight being sufficient to kill a rabbit when injected subcutaneously; this is much more poisonous than Cushny's preparation. Cushny's results are in the main confirmed; there is little ground for believing that ricin is a non-proteid substance.
W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Physiology of *Bacillus Prodigiosus*. S. SAMKOW (*Centr. Bakt. Par.*, 1903, ii, 305—311).—The appearance of the red pigment during the growth of *Bacillus prodigiosus* is conditioned by the presence of magnesium salts in the nutrient material, although there is no magnesium in the pigment itself.

A. McK.

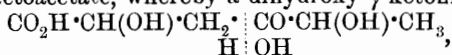
Buckwheat in presence of a Mixture of Algæ and Bacteria. RAOUL BOUILHAC and ERCOLE GIUSTINIANI (*Compt. rend.*, 1903, 1274—1276).—Sand cultures (2·5 kilos. of sand) of *Nostoc punctiforme* and *Anabaena*, with bacteria, gained 37 mg. of nitrogen in six weeks, the gain in sand alone, attributed to rain, being only 4 mg. of nitrogen.

Experiments were also made in which buckwheat was grown in pots containing sand (10 kilos.) free from organic matter. One pot remained without inoculation, whilst two received small quantities of

algæ and a few drops of soil extract. The algæ and bacteria enabled the buckwheat to grow normally; in absence of algæ, the growth was very restricted.

N. H. J. M.

The Chemical Reactions Occurring during Alcoholic Fermentation. EDUARD BUCHNER and JAKOB MEISENHEIMER (*Ber.*, 1904, 37, 417—428).—A number of experiments have been made to determine the amounts of lactic acid in (a) fresh yeast extract, (b) the same extract when kept for several days, (c) the same extract after addition of sucrose and keeping, and (d) the same extract after addition of *i*-lactic acid. Although all the results do not agree, it is concluded that α -lactic acid plays an important part in alcoholic fermentation, and is probably an intermediate product of the decomposition. A modification of Baeyer's hypothesis (*Ber.*, 1870, 3, 73) is suggested; the first process is regarded as a hydrolysis similar to the ketonic hydrolysis of ethyl acetoacetate, whereby a dihydroxy- γ -ketonic acid,



is formed, and this, on further hydrolysis, yields α -lactic acid.

The differences in the results obtained with different yeast extracts; in the one case, an increase, and in the other a diminution in the amount of lactic acid present after keeping, is explicable if it is assumed that two enzymes are concerned, one of which transforms the dextrose into lactic acid and the other decomposes the lactic acid into alcohol and carbon dioxide.

Acetic acid is also formed during alcoholic fermentation with yeast cell extract.

All extracts used were previously mixed with 1 per cent. of toluene.

J. J. S.

Plants containing, in their Seeds, an Enzyme which Decomposes Fats into Glycerol and Fatty Acids. SERGIUS FOKIN (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 831—835).—The author has examined the seeds of several plants for the presence of an enzyme capable of decomposing fats into glycerol and fatty acids. The seeds of *Chelidonium majus* are especially active in this respect, more so, indeed, than those of the castor oil plant. The enzyme was also detected, although in less quantity, in the seeds of *Taraxacum vulgare*, *Brunella vulgaris*, *Cynoglossum*, *Aquilegia vulgaris*, and *Aconitum Lycoctonum*.

T. H. P.

Rôle of Calcium Oxalate in the Nutrition of Plants. AMAR (*Compt. rend.*, 1903, 137, 1301—1303).—The results of experiments with different plants indicated that calcium (supplied in the form of nitrate) is entirely assimilated up to a certain point, which varies according to the species of plant, and that any excess is eliminated as oxalate. The conclusion is drawn that calcium oxalate is formed to eliminate calcium and not, as supposed by Böhm, Schimper, and Groom, to eliminate oxalic acid.

N. H. J. M.

Development of Annual Fatty Plants ; Study of the Mineral Bases. GUSTAV ANDRÉ (*Compt. rend.*, 1903, 137, 1272—1274).—The amounts of water, calcium, and potassium were determined at successive periods of growth in *Sedum azureum*, *Mesembrianthemum tricolor*, and *M. crystallinum*. Whilst in *Sedum* there is an excess of calcium over potassium, the two *Mesembrianthemums* (especially *M. crystallinum*) contain a very large excess of potassium over calcium. The character of the fatty plant—the feeble transpiration and the low respiration—is not affected by the excess of potassium over calcium or the reverse.

N. H. J. M.

Acid of the Moss Berry. I. APARIN (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 811—815).—The acid contained in the moss berry (*Vaccinium oxycoccus* L.) was stated by Scheele (*Crell's Chem. Ann.*, 1785, 10, 291) to be citric acid, whilst according to Stolle (*Abstr.*, 1900, ii, 614) it is glyoxylic acid. The author finds that the only acid present in the moss berry is citric acid, the aldehydic properties of the acid obtained by Stolle being probably due to admixed dextrose.

T. H. P.

Relation between the Amounts of Gluten and Total Nitrogen in Different Wheats. ÉMILE FLEURENT (*Compt. rend.*, 1903, 137, 1313—1315).—The results of analyses of seventeen varieties of wheat show that the relation of gluten to total nitrogenous matter frequently varies. Wheats which contain the same amounts of total nitrogen may show variations in gluten of 1.3 to 1.82 per cent., and wheats containing the same amounts of gluten may vary, as regards the amount of total nitrogenous matter, by 0.4 to 3.26 per cent. The variation is chiefly due to differences in the relation of envelopes and germs in the different varieties. Richness in gluten is not incompatible with the yield and is mainly a question of variety.

Determination of total nitrogen is insufficient and should be replaced by determination of gluten, on which the value of the mill-products depends.

N. H. J. M.

Composition of Different Parts of the Maize Kernel. CYRIL G. HOPKINS, L. H. SMITH, and E. M. EAST (*J. Amer. Chem. Soc.*, 1903, 25, 1166—1179. Compare *Abstr.*, 1899, ii, 687).—The amounts of proteids, carbohydrates, oil, and ash were determined in the separated portions (tip caps, hulls, horny gluten, horny starch, crown starch, tip starch, and germs) of low, medium, and high protein grain.

The hulls contain the lowest percentage (about 4) of proteids, then the tip caps and white starchy parts. The germs are very similar as regards percentage of proteids, those of the low proteid grain containing rather more than those of the high proteid grain. The germs contain most of the oil and about 10 times the average percentage of ash of the other parts of the grain.

As regards the percentage amounts of the different parts of the low, medium, and high proteid grain, the tip caps, hulls, and germs increase with the increase of proteids in the entire grain, whilst crown starch and tip starch decrease. The horny gluten is lowest in the

medium and highest in the high protein grain, and the horny gluten highest in the medium and lowest in the low protein grain. These discrepancies disappear if the two horny parts are considered as one.

The following table shows (1) the percentage of proteids in the grain and (2) the distribution of the proteids in (a) low, (b) medium, and (c) high proteid grain.

| | Proteids per cent. | | | Distribution of proteids. | | |
|-----------------|--------------------|-------|-------|---------------------------|--------|-------|
| | (a). | (b). | (c). | (a). | (b). | (c). |
| Tip caps | 0.09 | 0.13 | 0.08 | 0.89 | 1.14 | 0.59 |
| Hulls | 0.27 | 0.23 | 0.23 | 2.75 | 2.07 | 1.85 |
| Horny part ... | 5.25 | 6.69 | 8.20 | 53.07 | 59.03 | 64.88 |
| White starch... | 2.37 | 2.00 | 1.80 | 23.98 | 17.63 | 14.22 |
| Germes | 1.91 | 2.28 | 2.33 | 19.31 | 20.14 | 18.45 |
| | 9.89 | 11.33 | 12.64 | 100.00 | 100.01 | 99.99 |

N. H. J. M.

Status of Phosphorus in Certain Food Materials and Animal By-products, with Special Reference to the Presence of Inorganic Forms. EDWIN B. HART and WILLIAM H. ANDREWS (*Amer. Chem. Journ.*, 1903, 30, 470—485).—Commercial feeding-stuffs of vegetable origin do not contain appreciable amounts of inorganic phosphorus. The same holds good in the case of animal foods with the exception of meat meal, which may contain more or less bone.

Germinated grains are rich in soluble organic phosphorus. The organic phosphorus of oats, maize, and wheat is not transformed into inorganic forms during germination (two weeks). Cow's fæces are not found to contain inorganic phosphorus.

N. H. J. M.

Amounts of Nitrogen and Organic Carbon in some Clays and Marls. NORMAN H. J. MILLER (*Q. J. Geol. Soc.*, 1903, 59, 133—140).—Analyses of soils are given to show that, under moist conditions, decaying vegetable matter in soil tends to become more nitrogenous, on account of the greater ease with which gaseous compounds are formed with carbon than with nitrogen. In samples of clays and marls, taken from deep borings in various strata from the London Clay to the Lower Lias, the amount of calcium carbonate varied from 82.1 to 0 per cent., organic carbon from 1.299 to 0.299, and nitrogen from 0.069 to 0.021; the highest proportion of organic carbon to nitrogen was 40.6 : 1, and the lowest 8.8 : 1.

L. J. S.

The Potassium of the Soil Soluble in Water and its Utilisation by Plants. THEOPHILE SCHLOESING, jun. (*Compt. rend.*, 1903, 137, 1206—1209. Compare *Abstr.*, 1902, ii, 220 and 626).—The potassium soluble in water was determined in four different soils in which maize had been grown, and in samples of the same soils kept under the same conditions, but without vegetation. The uncultivated soils were found to contain an excess of potassium soluble in water,

as compared with the corresponding samples which had grown maize, the difference being, in one case, exactly the same as the amount of potassium contained in the maize plant, and in the other three cases somewhat less than the amounts accounted for by the maize.

N. H. J. M.

Analytical Chemistry.

Extract of Iris Flowers as a Sensitive Indicator. A. OSSENDOWSKY (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 845—846).—By quickly washing the flowers of the Japanese iris (*Iris Kaempferi*) with cold water, and then heating a pound of the flowers on the water-bath with 500 c.c. of water for 3—4 hours, a dark violet solution is obtained which gives very sharp colour changes with acids and alkalis. With mineral acids, it becomes bright red; with organic acids, crimson-red; with alkalis, emerald-green; and with organic bases, bright green. T. H. P.

Efficient Asbestos or Graphite Muffle. JAMES M. PICKEL and C. B. WILLIAMS (*J. Amer. Chem. Soc.*, 1903, 25, 1277—1280).—A small muffle is described suitable for heating a single dish or crucible. It consists of a cylindrical receptacle with an internal diameter and height each of 9.5 cm. which is attached to an asbestos cylinder, 3.5 cm. high and 3.5 cm. in internal diameter; the latter fits on to an Argand burner, and is provided with a slot or hole through which the flame can be observed. The crucible to be heated is placed on a pipe-clay triangle within the receptacle, which is closed by a cover composed of asbestos, a plate of aluminium, and a sheet of platinum riveted together, the asbestos forming the top of the lid and the platinum the bottom; this lid is provided with a hole of about 3 cm. diameter.

The muffle can be made of asbestos board about 6 mm. thick, by soaking it in water, rolling it round a suitable core, and allowing it to dry. The lower cylinder is then fitted in and the whole bound together with wire. A more durable form can be made of graphite coated with an asbestos jacket. The lid also can be made of graphite. The muffle can be used with a Bunsen burner by supporting it on a tripod.

The author employs a battery of twelve of these small muffles for expelling the ammonium salts in the estimation of potash in fertilisers; it has the special advantage that from one to twelve estimations can be carried out simultaneously, each under separate control.

E. G.

Calculation of the Results of Gas Analyses. ALFRED WOHL (*Ber.*, 1904, 37, 429—433).—It is pointed out that, taking the latest

values for the mol. volumes of different gases, for example, on the basis $O=1$, $H_2=1.0017$; $CO=1.0000$, $CH_4=1.0020$; and $CO_2=0.99393$ (Rayleigh, *Proc. Roy. Soc.*, 1898, 62, 204), Avogadro's hypothesis is only approximately correct, and that in accurate gas analyses this must be taken into consideration, and the calculations must be based on the actual molecular volumes.

Thus, in estimating hydrogen, carbon monoxide, and methane, where K =contraction, CO_2 the carbon dioxide formed, and O the oxygen used.

$$\begin{aligned} H_2 &= 0.6670 K \text{ and not } 2/3 K. \\ &= 2.0034 O \quad \text{,,} \quad 2 O. \\ CO &= 1.9760 K \quad \text{,,} \quad 2 K. \\ &= 1.0061 CO_2 \quad \text{,,} \quad 1 CO_2. \\ CH_4 &= 0.4990 K \quad \text{,,} \quad K/2. \\ &= 1.0082 CO_2 \quad \text{,,} \quad 1 CO_2. \\ &= 0.5010 O \quad \text{,,} \quad O/2. \end{aligned}$$

When hydrogen, carbon monoxide, and methane are estimated together by combustion with air through a capillary tube, the equations become

$$\begin{aligned} H_2 &= 1.0005 K - 1.0017 O - 0.0060 CO_2. \\ CO &= 0.3329 K - \quad \quad \quad O - 1.3394 CO_2. \\ CH_4 &= -0.3336 K + 1.0020 O - 0.3340 CO_2. \end{aligned}$$

For ordinary work, these equations may be taken as:

$$\begin{aligned} H_2 &= K - O - 0.006 CO_2; \\ CO &= K/3 - O + 3/4 CO_2 + 0.006 CO_2; \\ CH_4 &= -K/3 + O - CO_2/3. \end{aligned}$$

J. J. S.

Complete Gas Analysis by means of Pressure Measurements. ALFRED WOHL [with EICKMANN] (*Ber.*, 1904, 37, 433—451. Compare *Abstr.*, 1903, ii, 39).—Complete gas analyses may be conducted by an extension of the method previously described. Descriptions of the most convenient methods of filling the flasks and of passing the gas from one flask to another are given. The unsaturated hydrocarbons may be absorbed by the aid of fuming sulphuric acid containing 5—7 per cent. of sulphuric anhydride. Hydrogen, carbon monoxide, and methane are estimated together by passing a mixture of the gas and air or oxygen through a Drehschmidt-Winkler platinum capillary tube and calculating the percentages from the contraction, the volume of carbon dioxide formed, and the volume of oxygen used (compare preceding abstract).

Full details as to method of procedure and calculation are given.

J. J. S.

New Method of Estimating the Halogen Elements in Organic Compounds. II. Chlorine and Bromine. HENRI BAUBIGNY and G. CHAVANNE (*Compt. rend.*, 1904, 138, 85—87).—In a previous paper (compare *Abstr.*, 1903, ii, 510), a method of estimating iodine in organic compounds was described which consists in oxidising the compound with a chromic acid mixture in the presence

of silver nitrate; in these circumstances, the chlorine and bromine are expelled and the iodine oxidised to iodate. If, however, the oxidation is effected in a long-necked flask provided with a ground-in glass stopper carrying two tubes, the one passing to the bottom of the flask and the other, shorter one, connected with a series of Liebig absorption bulbs charged with an alkaline solution of sodium sulphite, the escaping chlorine and bromine are retained in this solution and can be estimated in the usual way, whilst the iodine is retained as iodate in the mother liquor. In order to ensure complete absorption of the chlorine and bromine, the combustion must be conducted slowly, the last traces of the chlorine and bromine being removed from the flask by means of a current of air passing through the longer tube.

Results are given which show the accuracy of the method for the separation of bromine and iodine; a sketch of the distillation flask and absorption bulbs is also given. M. A. W.

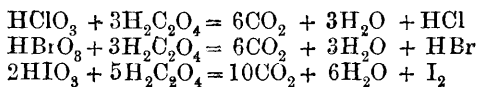
New Chlorometric Method. J. PONTIUS (*Chem. Zeit.*, 1904, 28, 59—60).—The method is based on the fact that a solution of sodium hypochlorite containing excess of sodium hydrogen carbonate quantitatively oxidises potassium iodide to iodate.

7.1 grams of bleaching powder are rubbed in a mortar with water, diluted to one litre, and 50 c.c. of the mixture are introduced into a flask containing at least 3 grams of sodium hydrogen carbonate. When the latter has dissolved, 1 c.c. of starch solution (free from iodide) is added, and the liquid is at once titrated with *N*/10 potassium iodide, 1 c.c. of which represents 0.00355 gram of available chlorine.

The process may also be applied to bleaching liquors, but as they generally contain alkali hydroxides or carbonates, these should first be neutralised by judicious addition of boric acid. One hundred c.c. of the liquid are then mixed with 6 or, if they are very weak, with 9 grams of sodium hydrogen carbonate and the solution is titrated as before.

L. DE K.

Estimation of Chlorates, Bromates, and Iodates. LÉON DÉBOURDEAUX (*Compt. rend.*, 1904, 138, 147—148).—When a solution of a chlorate, bromate or iodate is boiled with oxalic acid in presence of manganese sulphate and sulphuric acid, the following changes take place:



The above reactions are quantitative if certain precautions are taken; the solution must be made so as to contain 5 grams of manganese sulphate and 12 c.c. of concentrated sulphuric acid in every 100 c.c., moreover it is important that the temperature of the mixture should not be rapidly raised before boiling. After removing the halogen acids with silver nitrate, the oxalic acid remaining at the end of the operation can be titrated with permanganate. Having found

the amount of oxalic acid used, the chlorate, bromate, or iodate in the original solution can be calculated from the equations given.

S. S.

Use of Ferrous Sulphate in the Estimation of Chlorates and Bromates. ISAAC K. PHELPS (*Zeit. anorg. Chem.*, 1904, 38, 110—112).—A weighed quantity of the chlorate is heated to boiling in a covered flask with an excess of standardised ferrous sulphate solution (approximately $N/5$) and about 15 c.c. of sulphuric acid (1 : 4). The contents of the flask are then rapidly cooled, diluted to 600 c.c. with previously boiled water, and, after the addition of 2 grams of manganous chloride, titrated with potassium permanganate solution.

The same process is adopted in the case of bromates, except that the excess of ferrous sulphate is titrated with $N/10$ iodine solution in alkaline solution, instead of with permanganate in acid solution. After cooling, the contents of the flask are nearly neutralised by adding a concentrated solution of sodium carbonate. From 2 to 3 grams of sodium-potassium tartrate and an excess of $N/10$ iodine solution are added. The mixture is then treated with an excess of potassium hydrogen carbonate and titrated with $N/10$ arsenious oxide solution, using starch solution as indicator.

W. P. S.

Detection and Estimation of Hypochlorous Acid. EUTHYME KLIMENKO (*Zett. anal. Chem.*, 1903, 42, 718—724).—Hypochlorous acid mixed with potassium iodide liberates one atom of iodine for each molecule of HClO . On subsequent addition of hydrochloric acid, a second atom of iodine is set free. The equality of the two quantities of iodine is somewhat affected if the hypochlorous acid is added to highly concentrated solutions of potassium iodide, but by inverting the order and adding the iodide slowly to the hypochlorous acid, the difference practically disappears even with strong solutions. These reactions are not influenced by the presence of chlorine in the hypochlorous acid.

M. J. S.

Estimation of Sulphides and Haloids in presence of Each Other. WALTHER FELD (*Zeit. anal. Chem.*, 1903, 42, 708—711).—When no other sulphur compounds are present, the mixture may be distilled with magnesium sulphate in a current of carbon dioxide and the hydrogen sulphide received in a standard iodine solution. The haloid is thereafter precipitated from the residue in the retort. Another method is to precipitate both sulphide and haloid with an excess of silver, and estimate the unconsumed silver in an aliquot part of the solution; the precipitate, without washing, is then distilled with hydrochloric acid and aluminium clippings in an atmosphere of carbon dioxide, and the hydrogen sulphide estimated as before. The same method serves for the reduction of thionic acids to hydrogen sulphide. The sulphur of the polysulphides may be converted into thiocyanate by treatment with potassium cyanide. The haloids are estimated in a separate portion of the solution, after boiling with magnesia and mercuric oxide, which precipitates all the sulphur com-

pounds as mercuric sulphide. Should the original solution be alkaline, magnesium sulphate is added; acid solutions are neutralised with magnesia. Ammoniacal solutions must also be boiled with magnesia before adding the mercuric oxide.

M. J. S.

Rapid Estimation of Sulphur in Coal and Coke. J. D. PENNOCK and DARWIN A. MORTON (*J. Amer. Chem. Soc.*, 1903, 25, 1265—1269).—Sixteen grams of sodium peroxide and 0.7 gram of coal, or 11.5 grams of the oxide and 0.7 gram of coke, are carefully mixed with a spatula and introduced into a 40 c.c. nickel-plated, steel crucible, fitted with a lid perforated with a small hole for the introduction of a red-hot wire. The crucible is supported by a special stand placed in a beaker containing some water. The mass is fired, and after a few minutes the crucible is turned over into the water, which rapidly dissolves the fused mass.

After acidifying the solution, the sulphuric acid is estimated by the chromate process proposed by Andrews. [This consists in adding a solution of pure barium chromate in dilute hydrochloric acid, which precipitates the sulphuric acid with liberation of an equivalent amount of chromic acid; after precipitating the excess of barium chromate with ammonia, the chromic acid is estimated iodometrically.]

For a full description of both crucible and stand, the original article and illustrations should be consulted.

L. DE K.

Estimation of Nitrogen by Kjeldahl's Method. ROBERT BANKS GIBSON (*J. Amer. Chem. Soc.*, 1904, 26, 105—110).—Kutscher and Steudel obtained incorrect results when using the Kjeldahl process in the analysis of creatine, uric acid, and similar compounds. Their method was to heat the substance with sulphuric acid and a crystal of copper sulphate, and to complete the oxidation with potassium permanganate.

The author, however, by applying the well-known Kjeldahl-Gunning process (heating with sulphuric acid and potassium sulphate) has obtained perfectly satisfactory results in the case of the following substances. (The heating was always continued for a considerable time after the acid mixture became colourless.) Uric acid, hippuric acid, tyrosine, leucine, urethane, thiocarbamide, hydroxyphenylmethylpyrimidine, aminobenzoic acid, and caseinogen. In the case of substances of unknown structure, the results obtained by this process should, of course, be verified by the absolute method.

L. DE K.

A Burette, and Normal Solutions for Kjeldahl's Nitrogen Estimation. ALFRED W. BOSWORTH and WILHELM EISSING (*Zeit. anal. Chem.*, 1903, 42, 711—713).—By the use of a special burette and normal alkali, all calculations may be avoided. The burette, which is filled from below, is graduated from the bottom upwards. The acid is $N/2$, the alkali $N/14.04$, and 1 gram of substance is taken. For each c.c. of acid used for absorbing the ammonia, 7.02 c.c. of alkali is introduced into the burette, and the reading of the alkali burette, after the titration, divided by 10, gives at once the percentage of nitrogen.

M. J. S.

Gasometric and Gravimetric Estimation of Ammonia. E. RIEGLER (*Zeit. anal. Chem.*, 1903, 42, 677—686).—When treated with excess of iodic acid, ammonia or its salts form the tri-iodate, $(\text{NH}_4)\text{H}_2(\text{IO}_3)_3$, which is insoluble in dilute alcohol. This salt, when brought into contact with hydrazine sulphate, reacts according to the equation $2(\text{NH}_4)\text{H}_2(\text{IO}_3)_3 + 9\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4 = (\text{NH}_4)_2\text{SO}_4 + 8\text{H}_2\text{SO}_4 + 6\text{HI} + 18\text{H}_2\text{O} + 9\text{N}_2$, so that 1 c.c. of nitrogen (at 0° and 760 mm.) corresponds with 0.17 mg. of ammonia.

The ammonia solution (10 c.c. containing not more than 0.014 gram of N H_3) is mixed with 5 c.c. of a 20 per cent. solution of iodic acid and 25 c.c. of 95 per cent. alcohol. After an hour, the crystalline precipitate is collected on a small filter, and thoroughly washed with alcohol. The filter is then transferred to a cylinder attached to the bottom of a 200 c.c. flask, in the outer space of which there is placed 50 c.c. of a 2 per cent. solution of hydrazine sulphate. After connecting with a gas burette and equalising temperature and pressure, the flask is shaken until its contents, which at first are yellow, become colourless, and the volume of the nitrogen evolved is then read. The tri-iodate precipitate may also be collected on a weighed filter, dried over sulphuric acid in a desiccator, and weighed.

M. J. S.

Estimation of Hydrazine Free and Combined. ENRICO RIMINI (*Atti R. Accad. Lincei*, 1903, [v], 12, ii, 376—381).—When a solution of hydrazine sulphate is boiled in a Schultze-Tiemann apparatus with an excess of mercuric chloride, and, after eliminating the air, a little concentrated potassium hydroxide solution is added, the whole of the nitrogen of the base is evolved and can be measured; the action takes place quantitatively according to the equation $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4 + 6\text{KOH} + 2\text{HgCl}_2 = \text{K}_2\text{SO}_4 + 4\text{KCl} + 2\text{Hg} + \text{N}_2 + 6\text{H}_2\text{O}$. The amount of hydrazine in semicarbazides can be rapidly and accurately estimated in the same manner.

Conversely, mercuric chloride may be estimated by means of hydrazine. In the case of dilute solutions of the chloride, an excess of hydrazine sulphate is added and the foregoing operation in the Schultze-Tiemann apparatus carried out at the boiling temperature. With more concentrated solutions, it is better to work in the cold, using a Lunge or Knopp and Wagner's nitrometer.

W. A. D.

Estimation of the Nitrogen in Hydrazones and Osazones by Kjeldahl's Method. J. MILBAUER (*Zeit. anal. Chem.*, 1903, 42, 725—732).—The author confirms the statement of Dakin (*Abstr.*, 1902, ii, 533) that the addition of potassium persulphate is of great assistance in the oxidation of difficultly combustible organic substances by sulphuric acid. The process cannot, however, be employed directly for phenylhydrazine and its derivatives, in consequence of the tendency of these substances to evolve nitrogen when oxidised. After preliminary reduction by nascent hydrogen, the method can be applied with complete success. About 0.2 gram of the substance is mixed with 50 c.c. of water and 3 grams of zinc powder; 50 c.c. of concentrated

sulphuric acid are gradually added, and the mixture is gently boiled until reduction is complete. A drop of mercury is added, and the boiling is continued until the mixture is colourless. After cooling to about 100° , 2 grams of potassium persulphate are added, and the liquid is again heated for about half an hour. It is then neutralised with soda, a few grams more of the persulphate are added, and the ammonia is distilled off. M. J. S.

Estimation of Nitrites in the Absence of Air. ISAAC K. PHELPS (*Zeit. anorg. Chem.*, 1904, 38, 113—116).—The apparatus used is the same as that previously described for the estimation of nitric acid (Abstr., 1903, ii, 240). An excess of standardised arsenious oxide solution and 25 c.c. of concentrated sodium carbonate solution are placed in the flask and boiled for from 5 to 8 minutes to drive out all air. Seven c.c. of sulphuric acid (1:4) are then run in through the funnel, and the contents of the flask cooled. As the pressure in the flask approaches that of the outside air, the delivery tube is raised out of the mercury, but still kept under the surface of a layer of water on the mercury. The nitrite solution to be estimated is then added together with two grams of potassium iodide and sufficient sulphuric acid (1:4) to acidify the contents of the flask. A concentrated solution of potassium hydrogen carbonate is now run in until all free iodine has been combined, the mixture is boiled for five minutes to drive out nitric oxide, cooled, and titrated with $N/10$ iodine solution, using starch solution as indicator. W. P. S.

Estimation of Small Amounts of Arsenic in Paints, Wall-papers, &c. PETER KLASON and JOHN KÖHLER (*Bihang K. Svenska Vet. Akad. Handl.*, 1902—1903, 28, ii, No. 4, 1—18).—Like phosphoric acid, free arsenic acid may be estimated by titration with alkali. Using potassium hydroxide with methyl-orange as indicator, the solution shows a neutral tint when KH_2AsO_4 is formed, whilst with phenolphthalein this occurs when the solution contains K_2HAsO_4 .

With potassium iodate and iodide, arsenic acid acts as a monobasic acid, the reaction being: $\text{KIO}_3 + 5\text{KI} + 6\text{H}_3\text{AsO}_4 = 6\text{KH}_2\text{AsO}_4 + \text{HIO}_3 + 5\text{HI}$ and $\text{HIO}_3 + 5\text{HI} = 3\text{H}_2\text{O} + 3\text{I}_2$. The iodine may be determined by means of standard sodium thiosulphate solution. Small quantities (0.067—0.676 mg. of As_2O_5) of arsenic acid can be estimated in this way by using $N/500$ or $N/1000$ thiosulphate solution, but the titration must be carried out quickly and with vigorous shaking, as the liquid to which starch has been added very soon assumes a permanent blue colour, possibly owing to the action of the carbon dioxide of the air. The estimation of arsenious acid in small quantities after previous distillation with hydrochloric acid and oxidation with nitric acid does not give satisfactory results.

Mörner's method (Abstr., 1902, ii, 694) of estimating minute quantities of arsenic, which gives good results when applied to ochres and other colours, steel, copper, or wall-papers, gives very inaccurate results with woollen wares.

The dilute solutions ($N/500$ and $N/1000$) of sodium thiosulphate used by the author keep well. T. H. P.

Rapid Estimation of Boric Acid in Borax. K. JACOBI (*J. Amer. Chem. Soc.*, 1904, 26, 91—92).—Two or four grams of the sample are dissolved in water; excess of glycerol and a few drops of phenolphthalein solution are added and the free boric acid is titrated with $N/2$ potassium hydroxide. The result multiplied by 2 equals the total boric acid in the sample. L. DE K.

Estimation of Boric Acid as Phosphate. FRANZ MYLIUS and ADOLPH MEUSSER (*Ber.*, 1904, 37, 397—401).—The compound BPO_4 (G. Meyer, *Abstr.*, 1889, 108) may be considered as a mixed anhydride, boryl phosphate, $BO \cdot O \cdot PO_2$. Boric and phosphoric acids combine in sulphuric or acetic acid solution, or in acetic anhydride. Boric and phosphoric acids also combine when heated at 80—100°, forming a hydrated compound, *borylphosphoric acid*, $H_2(BO)PO_4$. The phosphate, prepared by either of these methods, is readily hydrolysed by water, but becomes inert after heating at 400°. At a white heat, the compound becomes distinctly crystalline.

In quantitative analysis, the boric acid is converted into methyl borate by distillation with methyl alcohol, phosphoric acid and an excess of ammonia are added to the distillate, and the whole is evaporated to dryness and ignited at 400° in a current of water-vapour, in which the ammonium phosphate and phosphoric acid volatilise, the residue being weighed as BPO_4 . The error may amount to 1 per cent., due on the one hand to slight volatilisation of the boryl phosphate, and on the other to imperfect removal of phosphoric acid. C. H. D.

Estimation of Alkalis in the presence of Borates. K. JACOBI (*J. Amer. Chem. Soc.*, 1904, 26, 88—91).—Silica is rendered insoluble as usual. The acid solution is precipitated with ammonia and ammonium oxalate, and the magnesium is then precipitated with ammonium phosphate. The phosphoric acid is now precipitated with ferric chloride and the excess of this removed by ammonia. The solution is freed from the bulk of ammonium salts by evaporation with 40 c.c. of nitric acid, and then again with 20 c.c. The residue is evaporated with excess of hydrochloric acid and finally brought to a dull red heat. The mass now consists of sodium (potassium) chloride, boric oxide, and regenerated sodium borate. After dissolving in water, the sodium existing as borate is titrated with $N/2$ sulphuric acid, using methyl-orange as indicator and the total boric acid is then titrated with $N/2$ potassium hydroxide in the presence of excess of glycerol, using phenolphthalein as indicator. The sum of the boric oxide and the sodium oxide subtracted from the total weight gives the sodium chloride, from which the sodium oxide is then found by calculation. Should potassium or sulphuric acid be present, these should be determined in a separate portion and allowed for. L. DE K.

Estimation of the Alkalis in Vegetable Substances. HUGO NEUBAUER (*Zeit. anal. Chem.*, 1904, 43, 14—36).—After a discussion of the inconveniences and deficiencies of the Fresenius method, the following process is proposed. The organic matter is oxidised and

removed by heating the substance with sulphuric and nitric acids in a Jena glass flask. The solution is evaporated in a platinum basin and the excess of sulphuric acid expelled. The residue is freed from silica by evaporation with hydrochloric acid, and is then dissolved in water and rinsed into a 125 c.c. flask. A quantity of milk of lime sufficient to yield a saturated solution of calcium hydroxide is added, the flask is filled up, and after half an hour the solution is filtered through a dry filter. An aliquot part (100 c.c.) is neutralised with $N/2$ oxalic acid, which at the same time indicates whether sufficient lime has been added. A little more oxalic acid is added, the mixture is heated to boiling, and made slightly alkaline with ammonia. The precipitate is washed with cold water containing ammonium oxalate. The filtrate is evaporated and ignited to expel ammonium compounds. The residue, which may contain traces of silica and alkali carbonates, is converted into normal sulphates by ordinary methods, and the potassium is estimated by platinic chloride, employing the author's modification of Finkener's method, which is applicable to the sulphates. Sodium is calculated from the difference. Special experiments showed that the removal of iron and phosphoric acid by calcium hydroxide involved no loss of alkali metals, also that in a saturated solution of calcium hydroxide, magnesium hydroxide is so slightly soluble that the weight of the alkali sulphates may be corrected by subtracting 0.5 mg. for the magnesium sulphate remaining. The solubility of calcium hydroxide is considerably increased by the presence of alkali sulphates, being nearly twice as much in a 2 per cent. solution as in pure water. Satisfactory results were obtained in test experiments.

M. J. S.

Determination of Free Lime and on so-called "Dead Burnt" Lime. EDWARD H. KEISER and S. W. FORDER (*Amer. Chem. J.*, 1904, **31**, 153—162).—A method is described for the estimation of free lime in Portland cement, basic phosphate slags, commercial quicklime, and similar substances, which is based on the fact that free lime combines almost instantly with water whilst basic calcium silicates are acted on much more slowly by water. A quantity of the substance, weighing 0.2—0.3 gram, is first heated in a platinum crucible to expel moisture, or, in the case of cements, is heated by means of the blow-pipe for a few minutes to expel carbon dioxide, and after cooling in a desiccator is again weighed. A few drops of recently boiled distilled water are added to the contents of the crucible, which is placed in a cylindrical brass receptacle provided with brass inlet and outlet tubes. This brass receptacle is then put into an air-bath and heated at 85° for about half an hour. A slow current of air, previously freed from moisture and carbon dioxide, is then drawn through the apparatus and the temperature raised to 185°. After the crucible has been thus heated for half an hour, it is transferred to a desiccator, and, when cold, is weighed. The increase is the weight of water which has united with the lime to form calcium hydroxide. A diagram of the apparatus is given.

It is generally supposed that when lime is very highly heated it becomes "dead-burnt" or inert to water, but experiments have shown

that pure lime which has been treated in this way slakes comparatively readily with warm water.

Lime combined with silica in proportions not exceeding 3 mols. of lime to 1 mol. of silica is only slowly acted on by water, and this method of estimating lime can therefore be employed in presence of the di- and tri-calcium silicates which are assumed to be present in Portland cements.

Aluminates are hydrated much more rapidly than silicates, and an allowance must therefore be made for the water with which they combine. The various calcium aluminates take up varying quantities of water, and the authors intend to study this subject. They conclude, however, from experiments already carried out, that if a Portland cement containing less than 10 per cent. of alumina takes up more than 3 per cent. of water, the excess is due to the free lime present.

E. G.

Estimation of Zinc in Zinc Dust. ALFRED WOHL [and EICKMANN] (*Ber.*, 1904, 37, 451—453. Compare de Koningk, *Abstr.*, 1903, ii, 758).—0.1788 gram of zinc dust is introduced into a flask of 100 c.c. capacity, fitted with stopcock. The temperature is kept at 20° and the pressure reduced by 700 mm. Five c.c. of hydrochloric acid of sp. gr. 1.1, containing a drop of platinic chloride solution are introduced. When the zinc is completely dissolved, the pressure is read off at the original temperature (compare *Abstr.*, 1903, ii, 39), and the percentage of metal is given by the formula $(700 - p) \times 2$, when 0.1788 gram of dust was taken for each 100 c.c. capacity of the flask.

J. J. S.

Volumetric Estimation of Zinc. W. GEORGE WARING (*J. Amer. Chem. Soc.*, 1904, 26, 4—29).—A lengthy article on the sources of error in the ordinary titration of zinc with ferrocyanide.

An important modification has been introduced in the analysis of zinc ores containing silica and heavy metals. The ore is decomposed with nitrohydrochloric acid (1 : 6), evaporated nearly to dryness with the addition of ammonium chloride, the residue is dissolved in water, and the filtrate boiled with a clean sheet of iron, or, better, aluminium, which precipitates the heavy metals. The filtrate is neutralised with sodium hydroxide, and then re-acidified with formic acid. From this solution, the zinc may be completely precipitated at 80° by cautiously passing a current of hydrogen sulphide until no further white precipitate is formed. The precipitate is collected and treated with dilute hydrochloric acid, which dissolves the zinc sulphide and leaves undissolved any cadmium sulphide which happens to be present. The solution of the zinc is mixed with some ammonium chloride and titrated with ferrocyanide. For other modifications and minute details necessary to ensure success, the original article should be consulted.

L. DE K.

Iodometry of the Precipitated Peroxides of Lead, Bismuth and Manganese. ERWIN RUPP (*Zeit. anal. Chem.*, 1903, 42, 732—735).—All attempts to precipitate lead, bismuth, and manganese

in the conditions of their definite hydrated peroxides, by the use of alkaline hydrogen peroxide, sodium hypochlorite, bromine dissolved in alkali or in acetic acid, or alkaline potassium persulphate gave precipitates of a lower and generally variable degree of oxidation. A lead precipitate having approximately the composition $9\text{PbO}_2 \cdot \text{PbO}$ was obtained with bromine in acetic acid solution, but when chlorides were present the precipitation was incomplete.

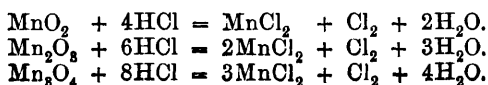
Manganese also yielded with alkaline persulphate a precipitate containing 95—96 per cent. of MnO_2 , but permanganate was formed if the precipitate was digested with the supernatant liquor for half an hour. The production of a definite peroxide precipitate seems to be possible only in cases where a solution acidified with a mineral acid can be used, as in Knorre's method for estimating manganese (Abstr., 1902, ii, 108). M. J. S.

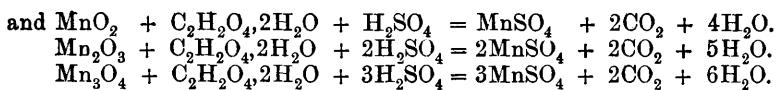
Solubility of Lead Sulphate in a Hydrochloric Acid Solution of Stannous Chloride. A. VAN RAALTE (*Zeit. anal. Chem.*, 1904, 43, 36—38).—The solubility of lead sulphate in a hydrochloric acid solution of stannous chloride (Abstr., 1903, ii, 108) is due solely to the hydrochloric acid present. M. J. S.

Detection of Mercury in Urine. ADOLF JOLLES (*Zeit. anal. Chem.*, 1903, 42, 716—718).—The author defends his method (Abstr., 1900, ii, 576) against the strictures of Schumacher and Jung, and considers that the failure of the latter to remove the mercury completely from the urine by a gilt platinum plate was due to some defect in the condition of the gilt surface (compare Abstr., 1903, ii, 696). M. J. S.

Method of Separating Aluminium and Iron by means of Formic Acid. ANDRÉ LECLERE (*Compt. rend.*, 1904, 138, 146—147).—The solution of iron and aluminium should be fairly dilute and acidified with sulphuric acid. Ammonium formate is added in large excess and the solution boiled with ammonium thiosulphate. This treatment reduces all the iron to the ferrous state, and precipitates the aluminium as basic formate. The latter is collected and converted into oxide by ignition, whilst the iron can be precipitated as sulphide from the solution. S. S.

Estimation of Manganese. LÉON DEBOURDEAUX (*Compt. rend.*, 1904, 138, 88—89).—The ordinary method of estimating manganese by determining (1) the amount of chlorine it liberates, and (2) the amount of hydrochloric acid necessary to furnish the chlorine, can be replaced by a much simpler process, involving the oxidation of oxalic acid by the higher oxides of manganese in the presence of warm dilute sulphuric acid. A comparison of the two series of equations





shows (1) that the chlorine liberated in the first series is equivalent to the oxalic acid destroyed in the second series, and (2) the hydrochloric acid used up in the first series is equivalent to the sum of the sulphuric and oxalic acids involved in the second series.

In estimating manganese by the new method, the specimen to be analysed is gently heated with a known volume of a standard solution containing 35—40 grams of oxalic acid and 120 c.c. of sulphuric acid of 66° Beaumé per litre; the oxalic acid in the residual liquid is then estimated by means of a standard permanganate solution, and the total free acids by means of a standard ammonia solution, using fluorescein as indicator; the differences between these two values and the corresponding values of the original solution give the necessary data for calculating the chlorine and hydrochloric acid equivalents of the oxide under investigation. M. A. W.

Employment of Persulphates for Quantitative Separations.

GEORG VON KNORRE (*Zeit. anal. Chem.*, 1904, 43, 1—14).—The statement of Dittrich and Hassel (*Abstr.*, 1902, ii, 693) that von Knorre's method for estimating manganese (*Abstr.*, 1902, ii, 108) can be applied under certain conditions to separate that metal quantitatively from calcium, magnesium, zinc, cadmium, copper, nickel, and aluminium, cannot be confirmed. In consequence of the acidic character of manganese dioxide, weighable, and sometimes considerable amounts of the other metals are invariably carried down, even when working strictly as Dittrich and Hassel prescribe. The estimation of the manganese is not thereby vitiated if the amount is ascertained by titrating the precipitate after destroying the excess of persulphate by prolonged boiling. Cobalt, lead, and silver interfere with this method by yielding peroxides. Chlorides must not be present in large amounts. The separation of manganese and chromium is, on the contrary, perfectly satisfactory, the chromic oxide being converted into chromic acid. M. J. S.

Standardisation of Permanganate. A. SKRABAL (*Zeit. anal. Chem.*, 1903, 42, 741—744).—With reference to the controversy between himself and Classen as to the purity of electrolytic iron deposited from an ammonium oxalate solution (*Abstr.*, 1903, ii, 684, 759), the author points out that Verwer in 1901 (*Abstr.*, 1902, ii, 693) showed that towards the end of the electrolysis carbonaceous iron is deposited, and that this fact invalidates the quantitative estimation of iron by electrolysis from Classen's solutions. Another impurity almost invariably present in Mohr's salt, which appears to have been overlooked by Classen, is zinc. In Classen's method, this impurity would tend to accumulate in the electrolytic iron, whereas in the author's it would not. M. J. S.

Iodometric Estimation of Uranium in Uranyl Compounds.

B. GLASMANN (*Ber.*, 1904, 37, 189—191).—Uranyl salts interact with Stock and Massaciu's iodide iodate mixture (*Abstr.*, 1900, ii, 247; 1901, ii, 284) according to the following equation: $3\text{UO}_2(\text{NO}_3)_2 + 5\text{KI} + \text{KIO}_3 + 3\text{H}_2\text{O} = 3\text{UO}_2(\text{OH})_2 + 6\text{KNO}_3 + 3\text{I}_2$. The reaction proceeds quantitatively in the course of a few minutes when the solution is warmed. It is necessary that the solution should be neutral or only very faintly acid. The liberated iodine is driven over with steam and absorbed in a receiver containing potassic iodide solution, which is kept well cooled, and this solution may then be titrated with standard thiosulphate. The whole operation takes some 20 minutes.

J. J. S.

Colour Reactions of Vanadic Acid and Vinyl Alcohol.

CAMILLE MATIGNON (*Compt. rend.*, 1904, 138, 82—84).—The rich blue coloration given by tannin and vanadic acid forms a very delicate test for the latter compounds, a solution containing 2 mg. of vanadium pentoxide per litre giving the blue colour. Similar colour reactions are given by gallic acid and pyrogallol; catechol gives a bluish-violet colour, but is a much less sensitive reagent than the other three; whilst resorcinol, quinol, guaiacol, and phloroglucinol give no coloration under the same conditions.

Commercial ethers which contain vinyl alcohol afford a more sensitive reagent for vanadic acid than any of the preceding compounds, since they give a rose coloration with solutions of ammonium vanadate or vanadic acid containing 1/10 mg. of vanadium pentoxide per litre. On allowing the ether to evaporate spontaneously, the residue becomes richer in vinyl alcohol and gives the characteristic rose colour with solutions containing 1/50 mg. per litre. That vinyl alcohol is the active principle in the ethers capable of giving the colour reaction was proved by the following facts (compare Poleck and Thümmel, *Abstr.*, 1890, 118): (1) the active ethers gave a white precipitate with a solution of mercuric chloride and potassium hydrogen carbonate, (2) they lost their activity after treatment with potassium hydroxide, which resinifies the vinyl alcohol, and (3) they became inactive after being shaken with water, which dissolves the vinyl alcohol.

M. A. W.

Estimation of Dissolved Gases in Sea-water.

ERNST RUPPIN (*Zeit. anorg. Chem.*, 1904, 38, 117—120).—The apparatus employed is that devised by Knudsen. It consists of a large, cylindrical bulb with a tube at the top and bottom. The upper tube is surrounded by a condenser, and above the condenser is closed by a 3-way tap, one opening of which connects with a funnel and the other with a gas-burette. The lower tube is joined to a mercury reservoir by means of tubing and is provided with a stop-cock. A side-tube, also fitted with a tap, is placed just above the stop-cock. After removing all air from the bulb by raising and lowering the mercury reservoir, a known volume (about 300 c.c.) of the sea-water contained in a sealed tube is admitted through the side-tube, one end of the sealed tube being broken under mercury and the other broken in the piece of india-rubber tubing by which it is connected to the

side-tube. The nitrogen and oxygen are driven off by gently heating the water in the bulb, a ring burner at the lower part of the latter being used for this purpose. The gases are collected in the gas-burette. After disconnecting the condenser, 5 c.c. of sulphuric acid of sp. gr. 1.125 are run in through the funnel and the heating continued at 100–105° until all carbon dioxide has been evolved. This gas is also collected in the gas burette, and the mixed gases analysed as usual. A correction for the 0.06 c.c. of oxygen and 0.04 c.c. of nitrogen contained in the 5 c.c. of sulphuric acid must be made.

W. P. S.

Estimation of Carbon Dioxide in Natural Waters. LUDWIG W. WINKLER (*Zeit. anal. Chem.*, 1903, 42, 735–740).—The total carbon dioxide of a natural water can be estimated by evolving hydrogen in the liquid and passing the mixed gases through an absorption apparatus. A stoppered bottle holding about 600 c.c. and of accurately known capacity is filled completely with the water to be examined, about 20 grams of granulated zinc having first been introduced. Into the neck of the bottle, a capacious cylinder is then fitted. This cylinder carries at the top a stopcock bulb and has a side-tube for conveying the gas to the potash bulbs. Boiled hydrochloric acid (50 c.c. of 18 per cent.) is placed in the bulb, a drop of platinic chloride is added, and the acid is gradually admitted to the apparatus. In about 3 hours, the whole of the carbon dioxide will have been carried over to the potash bulbs.

A new form of potash bulb which can be used ten times without refilling is described and figured.

M. J. S.

Estimation of Organic Matter in Water. Inconvenience of Filtration of Samples through Paper before Analysis. C. LENORMAND (*Bull. Soc. chim.*, 1904, [iii], 31, 139–141).—The author finds that in the passage of water through filter paper a certain amount of organic matter from the filter paper is dissolved by the water, and he suggests that determinations of “organic matter” should be made on unfiltered samples. The results of a number of determinations of “organic matter” in samples of sea and fresh waters before and after filtration through commercial filter papers are tabulated in the original.

T. A. H.

Estimation and Separation of Cyanogen Compounds and the Impurities contained therein. WALTHER FELD (*Chem. Centr.*, 1903, ii, 1398–1400; from *J. f. Gasbel.*, 46, 561–567).—*Alkali cyanides* are estimated in the presence of ferrocyanogen compounds by distillation with magnesium chloride, or, if the mass is likely to yield hydrogen sulphide, with a soluble lead salt; in either case, the hydrogen cyanide is quantitatively expelled and may be collected in aqueous sodium hydroxide and finally titrated with *N*/10 silver nitrate using potassium iodide as indicator.

Iron cyanogen compounds are decomposed by heating with an alkali hydroxide in the presence of mercuric chloride, and from the mercuric cyanide thus formed the hydrogen cyanide is liberated by distillation

with sulphuric acid. Insoluble iron cyanogen compounds are first triturated with aqueous potassium hydroxide, then treated at the boiling heat with magnesium chloride, and then with a sufficiency of mercuric chloride.

Sulphur Compounds.—The compounds usually present in crude cyanides are hyposulphites, polysulphides, thiosulphates, and thiocyanates. On distilling the mass with magnesium chloride in a current of carbon dioxide, the hydrogen sulphide is expelled and may be titrated with standard iodine and thiosulphate; the inhibiting action of the hydrogen cyanide may be prevented by adding hydrochloric acid before titrating with the thiosulphate. Any sulphur existing as polysulphide separates as such and may be collected as usual. *Thiosulphates* and *thiocyanates* are quantitatively reduced to hydrogen sulphide by the action of sheet aluminium and hydrochloric acid. The separation of *thiocyanates* and *thiosulphates* is best effected by boiling with a mixture of mercuric and magnesium chlorides with magnesium oxide; this does not affect the thiocyanate, which may then be reduced as before with aluminium.

Analysis of "Crude Cyanogen." In the estimation of the cyanogen not in combination with iron, an aliquot part of the cold aqueous solution (to which a little magnesium chloride has been added) is precipitated with lead nitrate and the hydrogen cyanide is distilled off as previously directed. For the estimation of the soluble iron cyanogen compounds, the cyanogen of the alkali cyanides is first expelled by means of magnesium chloride, the hot liquid is then treated with sodium hydroxide and mercuric chloride, and, after boiling, the mercury cyanide is decomposed by distillation with sulphuric acid. For the determination of the insoluble iron cyanogen compounds, the alkali cyanides are first decomposed by evaporation with magnesium chloride, the mass is then treated with strong aqueous sodium hydroxide, boiled with addition of mercuric chloride, and finally distilled with addition of sulphuric acid, allowing, of course, for the soluble ferrocyanide. Sulphur compounds are estimated as previously directed. Thiosulphates only occur in very bad samples of gas-purifying material.

L. DE K.

Estimation of Glycerol in Wine. JOSE G. GUGLIELMETTI and VICTOR COPPETTI (*Ann. Chim. anal.*, 1904, 9, 11—12).—Fifty grams of clean sand and 2.5 grams of animal charcoal are well mixed, 50 c.c. of wine are added, and the whole evaporated to dryness on the water-bath. After intimately mixing the mass with 5 grams of calcium oxide, the whole is extracted on the water-bath first with 50 and then twice in succession with 25 c.c. of absolute alcohol. The united filtrates are concentrated to 5 c.c., transferred to a tube, the dish is washed first with another 5 c.c. of alcohol, and then with 30 c.c. of pure ether. The whole is well shaken, allowed to settle, and filtered. The ethereal alcoholic liquid is then evaporated in a dish furnished with a close-fitting lid, the residual glycerol is dried for 45 minutes at 60—70°, cooled under a desiccator, and weighed.

L. DE K.

Sodium Monosulphide as Indicator in the Estimation of Dextrose with Fehling's Solution. L. BEULAYGUE (*Compt. rend.*, 1904, 138, 51—53).—The titration of dextrose or any reducing sugar

with Fehling's solution is often rendered inaccurate by the difficulty of obtaining a sharp end point to the reaction. This is especially the case when estimating the reducing sugars in diabetic urines. To overcome the difficulty, the author proposes the use of sodium monosulphide as an indicator. The method of titration and the precautions taken during the process are the same as those usually adopted. When the end of the reaction is approached, a drop of the titrated liquid is taken out and placed on a double piece of filter paper; the upper layer retains the cuprous oxide and allows some of the liquid to pass through to the lower sheet. A drop of the sulphide solution (10 parts of water to one part of crystallised sodium monosulphide) is placed in contact with the solution in the second layer of filter paper; if copper is present, a black or brown stain of copper sulphide is formed. By repeating this process at intervals during the titration, a point is reached when the sulphide fails to produce any colour even when the paper is examined by transmitted light. When this is attained, the reduction of the Fehling's solution is complete.

It is important that the Fehling's solution used should be standardised by the same method. S. S.

Estimation of Raffinose. DAVID L. DAVOLL, jun. (*Zeit. Ver. deut. Zucker-Ind.*, 1903, 1041—1049).—The author has examined the various methods proposed for the estimation of raffinose in presence of sucrose, and finds that the method of inversion according to Clerget's directions gives the best results. It is best, however, to use as the clarifying material, not animal charcoal, but powdered zinc, which is allowed to act on the inverted solution at the temperature of inversion (69°). After cooling the liquid to 20°, the zinc should be filtered off by means of a plug of cotton-wool, which must, of course, be thoroughly washed; as, if the zinc is left in the solution, the continuous evolution of hydrogen prevents the liquid from being made up exactly to volume. T. H. P.

The Composition of Linseed Oil and the Estimation of the Saturated Fatty Acids. WILHELM FAHRION (*Zeit. angew. chem.*, 1903, 16, 1193—1201).—A lengthy article dealing chiefly with Mulder's investigations (1867). The composition of linseed oil may be fairly expressed as follows: unsaponifiable, 0·8; palmitic and myristic acids, 8·0; oleic acid, 17·5; linoleic acid, 26·0; linolenic acid, 10·0; isolinolenic acid, 33·5; glycerol-residue (C_3H_2), 4·2. L. DE K.

Estimation of Unsaponifiable Matters in Linseed Oils. CARL NIEGEMANN (*Chem. Zeit.*, 1904, 28, 97).—The author has tested 18 specimens of undoubtedly genuine linseed oil and finds the amount of unsaponifiable matter to vary from 0·74 to 2·15 per cent. A very low percentage does not necessarily indicate a superior article. The estimations were made by Allen and Thomson's ether process (*Chem. News*, 1881, 43, 267). L. DE K.

Some Indian Oils. JULIUS LEWKOWITSCH (*Analyst*, 1903, 28, 342—343).—*Pongam Oil*.—Obtained from pongam beans, the fruit of

Pongamia glabra, Vent., a tall tree growing all over East India. At 15°, the oil is a buttery mass of a dirty yellow colour. Two samples gave the following figures: sp. gr. 0.9352—0.9240 at 40°/40°; saponification number, 178—183.1; iodine number, 94.0—89.4; Reichert-Meissl number, 1.1; unsaponifiable matter, 9.22—6.96 per cent.; refractometer number, 78.0—70.0; free fatty acids (as oleic), 3.05—0.5 per cent. The first values were given by a sample extracted in the laboratory with ether; the second by a specimen obtained from India.

Margosa Oil.—This oil is obtained from the seeds of *Melia azedarach*, a large tree cultivated throughout India and Burma. It has a sp. gr. of 0.9023 at 40°/40°; saponification number, 196.9; iodine number, 69.6; Reichert-Meissl number, 1.1; refractometer number, 52. The oil is solid at the ordinary temperature.

Ben Oil.—A genuine sample gave a sp. gr. of 0.9127 at 15°/15°; iodine number, 72.2; and refractometer number, 50.0. A solid portion of oil of ben separated by filtration at 0° had an iodine number 109.9, whilst that of the liquid portion was 111.8.

W. P. S.

Analysis of Urine. EMIL C. BEHRENDT (*Chem. Zeit.*, 1903, 27, 1270—1271).—*Uric Acid*.—Precipitation with barium chloride leads to erroneous results. Direct precipitation with hydrochloric acid is also incomplete. Ruhemann's iodine titration process (Abstr., 1902, ii, 435) gives very indifferent results with made up solutions of uric acid, but with urines the results agree fairly well with Salkowski's standard process, being, however, from 0.0038—0.0112 per cent. too low. Very good results may be obtained by Tunnicliffe and Rosenheim's volumetric piperidine process (Abstr., 1898, ii, 196).

Urea.—Riegler's process with Millon's reagent in a special apparatus (Abstr., 1897, ii, 390) is recommended.

Indican.—Ellinger's process (Abstr., 1903, ii, 620) is up to the present the most trustworthy process, as about 85 per cent. of the indoxyl is converted into indigo, but it requires time. L. DE K.

Reaction of Cryogenine. GUSTAVE PATEIN (*J. Pharm. Chim.*, 1903, [vi], 18, 593—594).—By mixing 1 c.c. of forty per cent. formaldehyde solution with 1 gram of cryogenine (*m*-semicarbazidobenzamide, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}_2$), dissolved in alcohol, diluting with water and then adding 2 or 3 drops of hydrochloric acid, a white powder is precipitated quantitatively. The product is very sparingly soluble in alcohol, ether, or chloroform, and seems to be acted on by carbon disulphide. It commences to melt and becomes coloured at 205°.

The method does not give completely satisfactory results in the estimation of cryogenine in urine, and as a qualitative test, is not so characteristic as the green coloration and reduction on boiling with Fehling's solution. G. D. L.

Estimation of Morphine in Opium and Tincture of Opium. EDWIN DOWZARD (*Pharm. J.*, 1903, [iv], 17, 909—910).—Eight grams

of the sample are treated with 100 c.c. of water in a closed flask for 1 hour at a temperature of 80—90° with constant agitation. The contents of the flask are then cooled, 3 grams of slaked lime are added, and the mixture again agitated for 1 or 2 hours. After filtration, 51.6 c.c. of the filtrate (equal to 4 grams of opium) are transferred to a corked flask, 5 c.c. of 90 per cent. alcohol, 30 c.c. of ether, and 2 grams of ammonium chloride are added, the flask is shaken for 30 minutes, and put aside for 12 hours. The contents of the flask are then poured on to a filter. The aqueous portion runs through, whilst the morphine remains attached to the filter, leaving the ether perfectly clear. The latter is removed by a pipette and the traces of morphine in the flask rinsed on to the filter with morphinated water. The filter and its contents are washed with morphinated water until free from chlorides, then once with 10 c.c. of distilled water, and finally with about 15 c.c. of ether, which after a few minutes is removed by a pipette. After being exposed to the air for 30 minutes, the filter and adhering morphine are placed in a beaker, broken up with a glass-rod, and gently heated with 20 c.c. of *N*/10 sulphuric acid solution. The mixture is now cooled and titrated with *N*/10 sodium hydroxide solution, using methyl-orange as indicator. Each c.c. of *N*/10 sulphuric acid is equivalent to 0.0283 gram of morphine, 0.05 gram being added to the weight of morphine found as directed in the B.P.

In the case of the tincture, 100 c.c. are evaporated to 30 c.c., cooled, 3 grams of slaked lime are added, and the mixture transferred to a 100 c.c. flask. Water is added up to the mark, any froth being removed by the addition of a drop of ether. Two c.c. of water are then added, and, after shaking for one hour, the contents of the flask are filtered. Fifty c.c. of the filtrate are operated on as described under opium.

Attention is drawn to a serious error in the B.P. method for estimating morphine in tincture of opium. Eighty c.c. of tincture and 3 grams of slaked lime are made up to 85 c.c. This volume should only be 81.9 c.c., as the 3 grams of lime together with extractive matter carried down by it displace 1.9 c.c. of water.

A table is given showing percentages of morphine in both opium and tincture of opium, for each 0.1 c.c. of *N*/10 sulphuric acid solution used, from 9 c.c. to 20 c.c.

W. P. S.

Estimation of Morphine in Opium. P. L. ASLANOĞLOU (*Chem. News*, 1903, 88, 286—287).—Ten grams of the powdered opium are thoroughly extracted with three successive quantities of about 150 c.c. of water, each extract being filtered and evaporated. The united dry residues are dissolved in 75 c.c. of water, filtered, and washed with water to make 100 c.c. of filtrate. To the latter, 30 c.c. of 94 per cent. alcohol are added, and after stirring for 30 minutes, 3 to 5 c.c. of 10 per cent. solution of ammonia. At the end of 12 hours, the mixture is poured on a tared filter, the precipitate is washed twice with 25 c.c. of water, and partly dried at a temperature of 60°. The filter and precipitate are then washed with ether, dried at 75°, and weighed.

To the weight of morphine found, 0.1012 gram is added to correct

for the solubility of morphine in the 184 c.c. of solution and wash-water employed. The true amount in the 10 grams of opium taken is then obtained.

W. P. S.

Localisation of Morphine in the Animal Organism. M. TORZE (*Chem. Zeit.*, 1903, 27, 1239—1243).—A review of work done by other investigators, together with some of the author's own experiments. The analytical process used was that of Marquis (final extraction of the morphine by means of ethyl acetate; testing for the alkaloid with sulphuric acid and formaldehyde).

The bulk of the unaltered alkaloid passes into the urine, and a perceptible amount is also found in the fæces. All other organs should, however, if necessary, be examined. The author could not detect morphine in the pancreas and bile.

L. DE K.

Van Deen's Reaction. NAZARENO TARUGI (*Gazzetta*, 1903, 33, ii, 216—222. Compare Abstr., 1903, ii, 460).—An aqueous solution of the oxydase of wheaten flour, although not losing its power of producing a blue coloration with tincture of guaiacum when exposed to a temperature of 50° for 2 hours, fails to respond to this test after an exposure of 25 minutes at 75°, but if after this treatment a few drops of old turpentine oil or of hydrogen peroxide solution be added, the blue coloration is at once reproduced. But if the oxydase is heated for another 25 minutes at 75° or 50 seconds at 100°, the power of producing the coloration, even after adding the solutions mentioned, is destroyed.

Similarly, an aqueous extract of maize flour, when heated for 10 minutes at 75° or for 10 seconds at 100°, loses its power of direct oxidation, and the same is true of bean flour when heated for a minute at 100°; in each case, this property is restored by the addition of the oxidising agents mentioned.

When egg-albumin is rapidly coagulated by adding it to water at 75° and the clear solution filtered from the coagulum, it does not directly colour tincture of guaiacum, but does so on adding hydrogen peroxide; it appears that the albumin contains an oxydase, which is destroyed by heat, but regenerated by the oxidising agent.

It is pointed out that not only the foregoing substances are capable of giving Van Deen's reaction, but also many aldehydes, and even acid anhydrides, owing to the formation of peroxide-like intermediate products.

W. A. D.

General and Physical Chemistry.

Spontaneous Emission of Light by Certain Uranium Salts. HENRI BECQUEREL (*Compt. rend.*, 1904, 138, 184—187).—The property possessed by certain radioactive substances of emitting light and heat energy has so far only been observed in the cases of radium and polonium; it is now found that certain salts of uranium are spontaneously luminous in the dark; the intensity of the luminosity appears to be constant, and to be most marked in the case of those salts which are rendered phosphorescent by the action of light. The most active salt in this respect is uranium potassium sulphate, some specimens of the double sulphates of uranium and sodium or ammonium are almost equally luminous, whilst crystals of the double uranium potassium chloride and one preparation of uranium ammonium oxalate emit a feeble light. Crystalline commercial uranium nitrate is distinctly luminous, whilst the phosphate and oxides of uranium and all the uranous salts, whether they are phosphorescent to light or the contrary, are not appreciably luminous under the conditions of the experiment. The luminosity of the active salts is not affected by preliminary exposure to the radiation from an electric arc, or to that of a radium salt, nor is it increased by placing the salts in contact with metallic uranium; it seems therefore to be due to the phosphorescence excited in the salt itself by the radiation emitted by the uranium it contains. The intensity of the luminosity as measured photometrically is about 20,000 times more feeble than that emitted by a specimen of radium chloride, the activity of which is about 10,000,000 times greater than that of the uranium salt. M. A. W.

Refractometric Studies Relating to the Constitution of some Cyanomethylenic Acids. ALBIN HALLER and PAUL T. MULLER (*Compt. rend.*, 1904, 138, 440—446).—The authors have determined the specific gravities and the specific refractions for the α , β , and γ -hydrogen lines and the D sodium line of the following alkyl cyanoacetoacetates: methyl cyanomethylacetoacetate, sp. gr. 0.8754 at $20^{\circ}/4^{\circ}$, n_D 0.2421; methyl cyanoethylacetoacetate, sp. gr. 0.8755 at $20^{\circ}/4^{\circ}$, n_D 0.2493; methyl cyanopropylacetoacetate, sp. gr. 0.8840 at $20^{\circ}/4^{\circ}$, n_D 0.2560; ethyl cyanomethylacetoacetate, n_D 0.2517; ethyl cyanoethylacetoacetate, n_D 0.2546; ethyl *n*-cyanopropylacetoacetate, n_D 0.2600; ethyl cyanoisopropylacetoacetate, n_D 0.2601; propyl cyanomethylacetoacetate, sp. gr. 0.8746 at $20^{\circ}/4^{\circ}$, n_D 0.2578; amyl cyanomethylacetoacetate, sp. gr. 0.8743, n_D 0.2672, ethyl cyanoacetonedicarboxylate, sp. gr. 0.8809 at $20^{\circ}/4^{\circ}$, n_D 0.2406; and of the following cyanomethylmalonic esters: ethyl cyanomalonate, sp. gr. 1.0931 at $20^{\circ}/4^{\circ}$, n_D 0.2345; ethyl cyanomethylmalonate, sp. gr. 1.0695 at $20^{\circ}/4^{\circ}$, n_D 0.2382; ethyl cyanoethylmalonate, sp. gr. 1.0521 at $20^{\circ}/4^{\circ}$, n_D 0.2439; ethyl cyanopropylmalonate, sp. gr. 1.0332 at $20^{\circ}/4^{\circ}$, n_D 0.2495.

Tables are given of the molecular refractions for the different rays and of the molecular dispersions between the α and γ -lines, and from

the results the following conclusions are drawn: (1) all the cyanoalkylacetoacetates have the same constitution, the difference between the values of M_D for consecutive members approximating to 4.60, the normal increment for CH_2 according to Brühl and Conrady; (2) the cyanoalkylacetoacetates have the enolic $[\text{RC}\cdot\text{OH}:\text{C}(\text{CN})\cdot\text{CO}_2\text{R}']$, and not the ketonic $[\text{RCO}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{R}']$ structure (compare Haller, Abstr., 1900, i, 372); (3) the approximately constant difference (about +1.5) between the observed and calculated values for the molecular refractions is to be attributed to the accumulation of negative radicles (2CO and CN) in the molecule (compare Abstr., 1900, i, 182; Muller, Abstr., 1902, i, 354; 1903, i, 77, 78, ii, 705); a further confirmation of this point is afforded by the fact that the cyanoalkylmalonic esters, which exist only in the non-enolic form, $\text{CN}\cdot\text{CR}(\text{CO}_2\text{R}')$ (compare Haller and Blanc, Abstr., 1901, i, 260), show similar constant differences between the experimental and calculated values for the molecular refractions.

M. A. W.

The Flame Spectra of the Alkali Metals. C. DE WATTEVILLE (*Compt. rend.*, 1904, 138, 346—349).—An examination of the photographs of the flame spectra of the alkali metals (lithium, potassium, and sodium) shows that the lines of the metals can be divided into two groups, (1) those which belong to the principal series and which are equally intense from all parts of the flame, (2) those which belong to the secondary series, and which are more intense from the lower part of the flame. These results are explained on the hypothesis, confirmed by experiment, that the flame is divided into zones, each of which emits only one group of lines, for if an image of the whole flame is thrown on to the slit of the spectroscope by means of a lens of short focal length, the resulting spectrum is divided longitudinally into three parallel bands; in the lower region, which corresponds with the blue cone, there are, in addition to the carbon bands, all the lines of the metal; in the upper region, which corresponds with the highest part of the flame, only the very strong lines of the principal series are seen.

M. A. W.

Radioactivity of the Atmosphere. S. J. ALLAN (*Phil. Mag.*, 1904, [vi], 7, 140—150).—It has been previously shown that a negative conductor becomes radioactive in the atmosphere, and that the rate of decay of the radioactivity is independent of the nature of the wire, &c. (Rutherford and Allan, Abstr., 1903, ii, 123). The radioactivity can be removed from the wire by rubbing it with a piece of felt or leather moistened with ammonia, which then itself becomes radioactive. The rate of decay of the radioactivity of the felt or leather is not, however, equal to that of the wire, and varies with the nature of the felt, but the radioactivity of the ashes of the felt decays at the same rate as that on the wire. The rate of decay of the radioactivity of the residue obtained by the evaporation of freshly fallen snow was found to be different from that of the atmospheric radioactivity. The absorption of various solids was determined, and the experiments indicate the existence of α -radiation, readily absorbed, and more penetrating than β -radiation, and this explains the differ-

ences between the behaviour of the felt and the wire, as in the former the α -rays would be largely absorbed before reaching the surface of the felt. The absorption in gases was also examined. The increase of the conductivity of air caused by a water spray (at Montreal) was not due to any emanation in the spray, but is produced by the mixture of the water spray with the air. The experiments indicate the complexity of the atmospheric radioactivity and the necessity of further investigation.

I. M. J.

The Emanation of Actinium. ANDRÉ DEBIERNE (*Compt. rend.*, 1904, 138, 411—414).—The energy of the emanation proceeding from actinium, when measured by the ionisation of a gas, is found to decrease regularly from the moment of its production. If the logarithms of the intensities of ionisation are plotted as abscissæ against the time which has elapsed since the production of the emanation as ordinates, a straight line is obtained, the inclination of which is determined by a constant. In the case of actinium, this constant = 3.9 seconds. The emanation of actinium also has the property of endowing other substances with radioactivity. The power of inducing radioactivity on other substances does not decay in the same way as the ionising energy of the emanation; for a short period after the production of the emanation, the exciting power increases until a maximum is reached, after which, however, it falls off at the same rate as the ionising energy. It seems, therefore, that the two effects, induction of radioactivity and ionisation of gases, are quite distinct from one another; from this point of view, the actinium emanation must be regarded as containing two different sources of energy.

The induced radioactivity of actinium decays quite regularly; after forty minutes from the instant of production, it has decreased to half its strength. Substances containing actinium seem to emit a second emanation, which decays much more slowly than the principal one described above.

S. S.

Heating Effect of the Radium Emanation. ERNEST RUTHERFORD and HOWARD T. BARNES (*Phil. Mag.*, 1904, [vi], 7, 202—222).—The experiments were conducted in order to determine how the heat emission of radium is connected with its radioactivity. For the measurement of the heat, a differential air calorimeter and platinum thermometers were employed; diagrams and descriptions of these are given. The emanation was driven off the radium bromide by heating, and was condensed in a tube surrounded by liquid air. The heating effect of the radium, when first tested, had fallen and continued to fall for about 3 hours, when it reached a minimum of about 30 per cent., after which it gradually increased, reaching its original value in about a month. Complementary changes were observed in the case of the emanation tube, so that the sum of the heating effects of the radium and the emanation tube during the whole course of the experiments was always equal to that of the original radium. The authors therefore conclude that about 75 per cent. of the heat is not due to radium directly, but to the emanation and the active matter it pro-

duces (termed emanation X). It was found that the curve of diminution of the heating effect of the emanation is nearly identical with the curve for the loss of radioactivity, and hence supports the view that the heat emission is an accompaniment of the expulsion of the α -rays. About 10 minutes after the removal of the emanation, the heating effect of radium is about 45 per cent. of the original; the gradual decay from this point to the minimum is due to the decay of activity of the "emanation X" left behind, and the curve was found to be similar to the decay to zero of the emanation tube after the removal of the emanation itself. The decay curves indicate 3 well-marked changes in the emanation X. In the first, half the matter is transformed in 3 minutes; in the second, half in 34 minutes; and in the third, half in 28 minutes. These changes will be discussed in a later paper, but the authors now state that the first is accompanied by α -rays, the second is not, and the third is accompanied by α -, β -, and γ -rays. The proportion of the heat effect due to the radium is about 25 per cent., that due to emanation and first change to emanation X, about 41 per cent., and that due to the second and third change about 34 per cent. The energy stirred up in the emanation is enormous, and the authors calculate that 1 c.c. would liberate per hour from 1.25×10^5 to 1.25×10^6 gram calories, and that 1 gram can radiate an amount of energy lying between 2×10^9 and 2×10^{10} gram calories.

L. M. J.

Influence of the Electric Discharge at Points on the Combination and Decomposition of Gases. ALEXANDRE DE HEMPTINNE (*Zeit. physikal. Chem.*, 1903, 46, 13—20).—Two similar tubes, connected on the one hand with a pump, and on the other with two separate manometers, are each provided with two platinum electrodes, a point and a disc. The tubes are filled with the same gas or gaseous mixture, and are so arranged that when the negative discharge takes place at the point in the one tube, it takes place at the disc in the other tube.

When the tubes are filled under low pressure with a mixture of hydrogen and oxygen, or a mixture of carbon monoxide and oxygen, combination takes place much more rapidly in the tube in which the point discharge is negative, the difference becoming more marked with diminishing pressure (compare Abstr., 1903, ii, 199). The synthesis of ammonia is slightly favoured by a negative point discharge, but the decomposition of ammonia and of carbon disulphide is not affected by the nature of the discharge so long as the pressure is greater than 5 mm. Whether a Wimshurst machine or a Ruhmkorff coil is the source of the electricity, it is found that the greater the difference in the light effects in the two tubes, the greater is the difference in the rates of combination; combination and decomposition appear to be effected especially in the luminous portions of the gas. J. C. P.

Dielectric Constants of Solvents and Solutions. HAROLD EVERETT EGGERS (*J. Physical Chem.*, 1904, 8, 14—36).—The dielectric constants were determined by the method employed by Drude (Abstr., 1897, ii, 438), and the following results were obtained;

| Substance. | Temperature. | Dielectric constant. | Substance. | Temperature. | Dielectric constant. |
|------------------------|--------------|----------------------|---------------------|--------------|----------------------|
| Methyl thiocyanate.. | 15.5° | 33.3 | Thiophen ... | 13.0° | 2.85 |
| Ethyl thiocyanate ... | 11.5 | 31.2 | Ethyl disulphide... | 19.0 | 15.6 |
| Amyl thiocyanate ... | 19.5 | 17.1 | Thioacetic acid ... | 21.0 | 17.3 |
| Methylthiocarbimide | 40.0 | 17.9 | Acetylacetone ... | 18.0 | 25.7 |
| Ethylthiocarbimide... | 15.0 | 22.0 | Acetyl methyl- | | |
| Allylthiocarbimide ... | 17.6 | 17.3 | hexyl ketone ... | 19.0 | 27.4 |
| Phenylthiocarbimide | 11.6 | 8.5 | Malononitrile ... | 32.6 | 46.3 |
| Amylhydrosulphide.. | 18.0 | 4.9 | Pinacolin ... | 17.5 | 12.6 |
| Phenylcarbimide ... | 17.0 | 3.36 | Nitroanisole ... | 19.8 | 23.8 |

In a homologous series, the dielectric constant decreases as the molecular weight increases. The high value for malononitrile appears to indicate that separation of the cyanide groups causes a rise of the dielectric constant, the value for cyanogen being 2.52 and for succinonitrile 61.2. The dielectric constants of solutions were then determined, the following being employed: sulphur, phosphorus, menthol, and camphor in carbon disulphide, menthol and camphor in benzene, and menthol in acetonitrile. It is found that the simple volumetric formula $[k = (k_1 v_1 + k_2 v_2)/(v_1 + v_2)]$ does not give even approximate values for the constant and is inapplicable.

When the same compound is dissolved in different solvents, the values indicate influence of the solvent; this the author considers to be probably due to the formation of indefinite compounds.

L. M. J.

Liquid Hydrogen Chloride as an Electrolytic Solvent.

DEMETRIO HELBIG and G. FAUSTI (*Atti R. Accad. Lincei*, 1904, [v], 13, 30—37. Compare Steele and McIntosh, *Proc.*, 1903, 220).—Liquid hydrogen chloride at its boiling point (-80.3°), under the ordinary pressure, has a specific conductivity 0.167×10^{-6} , which is approximately that of pure water; the conductivity is not changed by the addition of the chlorides of potassium, lithium, ammonium, copper, lead, platinum, gold and antimony, which are all insoluble in the liquefied gas. Stannic chloride dissolves in liquid hydrogen chloride but does not alter its conductivity. Ice cooled to -80° neither dissolves in the liquid nor changes the conductivity; on raising the temperature, the liquid boils, but the resistance remains constant.

For the details of the method used in the measurements, the original should be consulted; the hydrogen chloride was maintained at its boiling point by cooling it with a current of air which had been passed through a Dewar's vessel of liquid air.

W. A. D.

Electrical Conductivity of Solutions in Thiocyanates and Thiocarbimides. LOUIS KAHLBERG (*Zeit. physikal. Chem.*, 1903, 46, 64—69).—The solvents used and their specific conductivities were as follows: methyl thiocyanate, 7.38×10^{-6} ; ethyl thiocyanate, 4.8×10^{-6} ; amyl thiocyanate, 1.47×10^{-5} ; ethylthiocarbimide, less than 3.63×10^{-7} ; allylthiocarbimide, less than 4.3×10^{-8} . The

dielectric constants of these solvents have been determined by Eggers, and are respectively 33.3 (at 15.5°), 31.2 (at 11.5°), 17.1 (at 19.5°), 22.0 (at 15.0°), 17.3 (at 17.6°).

Most salts are insoluble in these substances, but ferric chloride, silver nitrate, mercuric chloride, trichloroacetic, and trichlorolactic acids were found to be soluble in the thiocyanates: ferric chloride and trichloroacetic acid are soluble also in the thiocarbimides, but these solvents are decomposed by silver nitrate and mercuric chloride. The solutions in methyl thiocyanate have the highest conductivity, and the thiocarbimide solutions have a low conductivity. The conductivity of ferric chloride in thiocyanates and thiocarbimides is much lower than in water or liquid hydrogen cyanide, and is of the same order as that in methyl and ethyl alcohols. The conductivity of silver nitrate in methyl and ethyl thiocyanates, and of mercuric chloride in ethyl thiocyanate is much lower than in aqueous solutions of corresponding strength. The conductivity of solutions of trichloroacetic acid in the thiocyanates and specially in the thiocarbimides is extremely low, and yet the solutions rapidly attack metallic magnesium or dry sodium carbonate.

J. C. P.

Electrical Conductivity of Aqueous Solutions at High Temperatures. I. Description of the Apparatus. Results with Sodium and Potassium Chlorides up to 306°. ARTHUR A. NOYES and WILLIAM D. COOLIDGE (*Zeit. physikal. Chem.*, 1903, 46, 323—378).—The authors have constructed a platinum-lined bomb of 124 c.c. capacity, provided with electrodes insulated where needful by quartz-crystal cylinders. Details of the construction of this apparatus are given in the paper. With this bomb, the conductivity and specific volume of aqueous solutions of sodium and potassium chlorides (from 0.1—0.0005 normal) have been determined at 140°, 218°, 281°, and 306°.

The variation of the dissociation with concentration at these temperatures is not that required by Ostwald's dilution law, any more than at the ordinary temperature. Of the various empirical expressions that have been proposed for the change of conductivity with concentration, that of Kohlrausch ($\Lambda_0 - \Lambda = KC^{\frac{1}{2}}$) is the most satisfactory. Barmwater's expression (Abstr., 1899, ii, 274) also gives good results, except at the highest temperature. To make applicable the general function $\Lambda_0 - \Lambda = K\Lambda^n C^{n-1}$, the value of n must be varied not only with the nature of the salt but also with the temperature.

The conductivity values extrapolated for infinite dilution vary with the temperature in an approximately linear manner, although there are deviations up to 3.5 per cent. in the case of potassium chloride at 281° and 306°. The temperature coefficients (referred to the values at 18°) are 3.05 per cent. for sodium chloride between 18° and 306°, 2.74 per cent. for potassium chloride between 18° and 218°.

The migration velocities of the potassium and sodium ions tend to become equal as the temperature rises, for the ratio of the con-

ductivities of the chlorides at infinite dilution decreases from 1.19 at 18° to 1.04 at 306°.

At the same temperature and concentration, the degrees of dissociation of sodium and potassium chlorides are nearly equal. The percentage dissociation in 0.1*N* solution is approximately as follows: 84 per cent. at 18°, 79 per cent. at 140°, 74 per cent. at 218°, 67 per cent. at 281°, and 60 per cent. at 306°. The change of dissociation with concentration is accurately given at all temperatures by the equation $(1-x)/C^{\frac{1}{2}} = K$. The conductivity of the vapour over a 0.1 *N*-solution of potassium chloride at 306° is certainly less than 1/200,000th part of that of the solution itself.

The specific volume of the 0.002 *N*-solutions (practically the same as that of pure water) was found to be 1.186 at 218°, 1.336 at 281°, and 1.434 at 306°. The expansions of the two 0.1 *N*-solutions agree very closely, but are somewhat less than that of water. For these solutions, the ratio of the specific volume at 306° to that at 4° is 1.422.

J. C. P.

Organic Solvent and Ionising Media. I. PAUL WALDEN (*Zeit. physikal. Chem.*, 1903, 46, 103—188. Compare Abstr., 1902, ii, 247).—To discover how far the views adopted in connection with the conductivity of water and aqueous solutions may be extended to other media, the author has made an exhaustive study of nearly forty organic solvents, including representatives of the alcohols, aldehydes, ketones, acids, acid anhydrides, chlorides, bromides, and amides, esters, nitriles, thiocyanates, thiocarbimides, and nitro-compounds. To facilitate comparison, one solute has been used throughout, namely, tetraethylammonium iodide.

The present paper deals exclusively with the solvents, and contains first a detailed account of investigations hitherto made on the conductivity of pure organic substances and their solutions. In describing his own work, the author lays stress on the purification of the various solvents, and shows how the degree of purity is evidenced by the conductivity. Successive fractions of a liquid distilling at a constant temperature have not the same conductivity. A minimum value for the conductivity of each solvent has been reached; thus, taking one or two common substances as examples: methyl alcohol, 1.45×10^{-6} ; ethyl alcohol, 1.985×10^{-7} ; acetone, 2.27×10^{-7} , all at 25°; acetaldehyde, 1.20×10^{-6} at 0°. In the majority of cases, the minimum value of the conductivity reached, which may be regarded as the characteristic conductivity of the substance, lies at 25° between 1×10^{-7} and 5×10^{-7} . The conductivity increases with the temperature, and the temperature coefficient varies with the class of substance. In homologous series, the first member has the highest conductivity. A few solvents are found to have an exceptionally high conductivity, for example, formamide, 4.7×10^{-5} ; acetamide (at 81°), 29×10^{-5} ; dimethylnitrosoamine, 3×10^{-5} ; acetylacetone, 1.6×10^{-5} ; formic acid, 1.5×10^{-5} ; values which approach those for fused electrolytes. The existence of a definite conductivity for each substance points to ionisation, and the author makes suggestions as to the ions probably present in each case.

In view of the parallelism suggested by Nernst and by Thomson between dielectric constant and dissociative power, the author has determined the dielectric constants of most of the solvents (and some other organic and inorganic substances) by Drude's method. He finds that the dielectric constants of acid, acid chloride, anhydride, and amide increase in the order given. The comparative effect of various substituent groups on the dielectric constant may be seen from the following values: $\text{CH}_3\cdot\text{NO}_2$, 38.2; $\text{CH}_3\cdot\text{CN}$, 35.8; $\text{CH}_3\cdot\text{CNS}$, 35.9; $\text{CH}_3\cdot\text{OH}$, 32.5; $\text{CH}_3\cdot\text{NCS}$, 19.7. Of the nitroparaffins and alkyl nitrates, the former have the higher values of the dielectric constant. The introduction of sulphur sometimes increases, sometimes diminishes the dielectric constant; compare $\text{CH}_3\cdot\text{CO}_2\text{H}$, 6.46; $\text{CH}_3\cdot\text{CO}\cdot\text{SH}$, 12.8; $\text{C}_2\text{H}_5\cdot\text{OH}$, 21.7; $\text{C}_2\text{H}_5\cdot\text{SH}$, 7.9. The dielectric constant is shown to be a markedly constitutive property, but in general it may be said that the passage from the first to the second member of a homologous series means a fall in the dielectric constant of about 50 units, whilst the passage from the second to the third member means a further fall of about 10 units.

J. C. P.

Ionisation caused by the Impact of Negative Ions of Incandescent Carbon. JOHANNES STARK (*Chem. Centr.*, 1904, i, 424; from *Phys. Zeit.*, 5, 51—57).—An ion which moves through a large difference of potential without collision may gain so much kinetic energy that it becomes able to ionise a neutral particle of gas by its impact. An electric discharge was passed through a gas contained in a glass globe, a metallic pin serving as anode and a \cap -shaped carbon filament as cathode. The latter was raised to incandescence; the high temperature caused strong electrification and ionisation at the surface of the cathode. The *E.M.F.* of ionisation was constant and not affected by temperature; for negative electron-ions in mercury vapour and in nitrogen, it was found to be 11 and 27 volts respectively.

The original paper also contains many other theoretical discussions and conclusions in regard to the influence of the surface of the solid on ionisation and current strength, secondary currents, &c.

E. W. W.

Hydrogen Peroxide Ions and their Discharge Potential. GIACOMO CARRARA and A. BRINGHENTI (*Gazzetta*, 1903, 33, ii, 362—371).—Measurements are given, with curves illustrating them, of the potential difference necessary to produce a current in normal solutions of sulphuric acid containing hydrogen peroxide. It is shown that in such solutions a current passes between a large, non-platinised platinum electrode covered with oxygen as the anode, and a platinum point as cathode at an *E.M.F.* of 0.26 volt, whereas under similar conditions in the same solution free from hydrogen peroxide, an *E.M.F.* of 1.08 volts is necessary. Making the large plate the cathode and the point the anode, the current passes at an *E.M.F.* of 0.39 volt in the presence of hydrogen peroxide, instead of 0.60 in its absence. The shape of the curves of cathodic polarisation plotted between *E.M.F.* and current indicate the existence of only hydrogen cations, and confirm the view that hydrogen

peroxide is a weak acid. It is probable that the anions are univalent $\cdot\text{HO}_2$, to which a discharge potential 1.47 volts is to be attributed.

W. A. D.

Effect of Ions on the Decomposition of Hydrogen Peroxide by Platinum Black. C. HUGH NEILSON and ORVILLE H. BROWN (*J. Amer. Physiol.*, 1904, 10, 225—228).—In general, the cation has an inhibiting or depressing effect, and the anion an accelerating effect.

W. D. H.

Effect of Ions on the Decomposition of Hydrogen Peroxide and the Hydrolysis of Ethyl Butyrate by an Aqueous Extract of Pancreas. C. HUGH NEILSON and ORVILLE H. BROWN (*J. Amer. Physiol.*, 1904, 10, 335—344).—The effect of certain salts in inhibiting the decomposition of hydrogen peroxide, and to a less degree the hydrolysis of ethyl butyrate by a pancreatic extract, can be explained by the hypothesis that the cations have a depressing and the anions an accelerating action.

W. D. H.

Experiments on Ionic Reactions. F. DUPRE (*Chem. Zeit.*, 1904, 28, 186).—No precipitate is formed when hydrochloric acid and a little barium chloride are added to an aqueous solution of potassium chromate; addition of sodium acetate diminishes the concentration of the hydrogen ions, and thus causes a precipitate. When a solution of copper sulphate and sodium chloride is boiled, the colour changes to green. The effect of dilution on solutions of copper chloride and cobalt chloride respectively was also studied. The separation of sulphur from a mixture of sodium thiosulphate and acetic acid, is prevented by the addition of sodium acetate.

A. McK.

The Influence of Complex Ions on Electrolysis by an Alternating Current. ANDRÉ BROCHET and JOSEPH PETIT (*Compt. rend.*, 1904, 138, 419—421).—It is shown that the presence of complex ions is not necessary to the action of an alternating current on a solution. This is supported by the mention of many cases where an alternating current produces changes in the composition of a liquid although the formation of complex ions is excluded. In all these instances, one or more of three phenomena are observed: (1) the evolution of electrolytic gas, (2) dissolution of electrodes, (3) oxidation or reduction. A few cases were examined where complex ions were present which are not decomposed by the ordinary continuous current. It was found that iron, cobalt, and platinum dissolve easily in aqueous potassium cyanide under the influence of an alternating current, giving potassium ferrocyanide, cobalticyanide, and platinicyanide respectively; if, however, the metals are used as anodes solution does not take place.

S. S.

Electrolysis with Alternating Current. MAX LE BLANC and K. SCHICK (*Zeit. physikal. Chem.*, 1903, 46, 213—243).—When a continuous current passes through a solution of sodium thiosulphate with cadmium electrodes, cadmium dissolves from the anode and forms

cadmium sulphide, whilst hydrogen is liberated at the cathode. With an alternating current of fairly high frequency, no cadmium sulphide is formed, but with lower frequencies the yield rises to as much as 77 per cent., when the contents of the cell are well mixed. That in these circumstances any cadmium sulphide at all is obtained is due to the removal of the dissolved cadmium from the reducing action of the next current impulse. The electrolysis of sodium thiosulphate with alternating current between silver or zinc electrodes gives similar results.

With an alternating current in a solution of potassium cyanide between copper electrodes, the question arises whether the copper that dissolves during one current impulse is reprecipitated on the electrode by the subsequent opposing impulse. If the copper ions have had time to form a complex with the potassium cyanide, the copper will remain in solution, and hydrogen will be liberated during the second current impulse. Actual experiments showed that in a $4N$ solution of potassium cyanide, with a current density of 4.6 amperes per square decimetre and any frequency up to 700 per minute, the copper went quantitatively into solution, and hydrogen was correspondingly liberated. With a frequency of 3400, 91 per cent. of the theoretical quantity of copper went into solution, with a frequency of 17,600, 58 per cent., and with a frequency of 38,600, 33 per cent. Contrast with this the result of electrolysing sodium hydrogen sulphate with an alternating current between copper electrodes. Copper forms no complex with hydrogen sulphate, and it is accordingly found that with a frequency of 1000 or upwards only very little copper goes into solution. With falling potassium cyanide concentration and diminishing current density, the amount of copper which goes into solution for a given frequency falls off; thus, in a $0.1N$ solution of potassium cyanide, with a current density of 2.3 and a frequency of 40,000, practically no copper goes into solution. The results as a whole show that the velocity with which the simple copper ions react to form the cyanide complexes is very great, but yet measurable.

Similar experiments have been carried out with silver, zinc, and nickel. Silver forms the complex $\text{Ag}(\text{CN})_2'$, but the metal can be liberated from this at the cathode, and so it is found that with a frequency of 1090 only 6 per cent. of silver is in solution. Zinc and nickel behave like copper, and in all three cases it appears that the velocity of reaction between the metallic ions and potassium cyanide is of the same order. The temperature-coefficient of this velocity is very small for copper, and even for zinc much smaller than is usual in chemical reactions. In order to obtain consistent results on the above lines, care must be taken that the electrodes have a crystalline appearance.

Other interpretations of the recorded phenomena may be suggested, but on the whole the explanation in terms of the reaction between copper and cyanide ions is the most suitable. J. C. P.

Use of Alternating Currents in Electrolysis. ANDRÉ BROCHET and JOSEPH PETIT (*Compt. rend.*, 1904, 138, 359—361).—Le Blanc and Schick (*Zeit. Elektrochem.*, 1903, 9, 636) have shown that the solubility

of copper in potassium cyanide under the influence of an alternating current, produced from a continuous current by means of a commutator, varies with the frequency, being quantitative for a frequency of 0.5 per minute, but diminishing as the frequency rises to 20,000 per minute [compare preceding abstract]. Similar results have been obtained by the authors using the current from a de la Rive electric sector with a frequency of 42; they find that the following equation represents the limit reaction: $\text{Cu}_2 + 8\text{KCN} + 2\text{H}_2\text{O} = \text{Cu}_2(\text{CN})_2 + 6\text{KCN} + 2\text{KOH} + \text{H}_2$. Zinc and nickel behave similarly, yielding double salts of the type $\text{M}(\text{CN})_2 \cdot 2\text{KCN}$, whilst lead, silver, mercury, or cadmium give no double salts.

M. A. W.

Reduction Phenomena produced by the Action of Alternating Currents. FRANCIS PEARCE and CHARLES COUCHET (*Compt. rend.*, 1904, 138, 361—362).—When certain saline solutions are subjected to the action of an alternating current, either the electrodes are dissolved as observed by Le Blanc and Schick, or the dissolved salts are more or less completely reduced; the latter phenomenon is dependent on the nature of the electrodes, those formed of readily oxidisable metals being the most effective, and also on the density and frequency of the current; with a current of low density, the electrodes only are oxidised, whilst with a high density current, the dissolved salt is also reduced. Solutions of ferric alum are only slightly reduced in the presence of platinum electrodes, much more reduced when electrodes of aluminium, lead, or cadmium are employed, whilst with iron electrodes the reduction is almost complete. Solutions of alkali nitrates are reduced quantitatively to nitrites with electrodes of cadmium or zinc, whilst with iron, copper, or carbon electrodes there is practically no reduction. Under similar suitable conditions, cupric salts are reduced to the cuprous state, mercuric to mercurous salts, or chromates to chromium salts, and nitrobenzene to a salt of aniline.

M. A. W.

Electrolytic Dissociation of Picric Acid. VICTOR ROTHMUND and KARL DRUCKER (*Zeit. physikal. Chem.*, 1903, 46, 827—852).—If it is assumed that picric acid in water obeys the mass action law (Ostwald's dilution law), and that there is a constant partition coefficient for undissociated picric acid between water and benzene, it can be shown by determining the distribution of picric acid between these two media that the mass action constant varies slightly but irregularly with the concentration, and has a mean value of 0.164 at 18°. An attempt was made to calculate the mass action constant for picric acid from freezing point depressions, but the experimental determinations are not sufficiently accurate to allow of this. When the degree of dissociation of picric acid is deduced from the conductivity of its solutions, the mass action constant varies markedly with the concentration. Attention is drawn to the great effect on the constant of a slight change in the value of λ_∞ , and in view of the validity of the mass action law, established for picric acid by the partition experiments, the results obtained from the freezing point or the conductivity are probably vitiated by experimental errors. The authors consider that the deviations of strong acids from the mass action law have been exaggerated.

J. C. P.

Influence of Non-electrolytes and Electrolytes on the Degree of Dissociation. MEYER WILDERMAN (*Zeit. physikal. Chem.*, 1903, 46, 43—63).—In the case of gaseous dissociation, the introduction of an indifferent gas does not affect the degree of dissociation, and the author shows that the analogous statement is valid in the case of electrolytic dissociation. With the help of the freezing point method, it is shown that the presence of a non-electrolyte (glycerol) does not appreciably affect the degree of dissociation of either dichloroacetic or *o*-nitrobenzoic acid. Further, the molecular depression of glycerol has the same constant value in the presence of either acid.

The mutual influence of two electrolytes with a common ion is discussed, and expressions are deduced whereby it is possible to calculate the degree of dissociation of each electrolyte, and thence to calculate the depression of the freezing point which should be observed in a solution containing both electrolytes. These deductions are tested and confirmed by experiments in which the freezing points of solutions containing nitric and *o*-nitrobenzoic acids have been determined.

J. C. P.

Experimental Law of Electric Transport of Dissolved Salts. AUGUSTE PONSOT (*Compt. rend.*, 1904, 138, 192—194).—From theoretical considerations based on Chassy's work on "A New Electric Transport of Dissolved Salts" (*Thèse de Doctorat*, 1890), the author deduces the two laws: (1) When in a mixture of salts of the same acid one salt only is electrolysed, the total number of molecules transported depends only on the nature and concentration of this salt, and is independent of the presence and concentration of the non-electrolysed salts. (2) When two salts are electrolysed, the total number of molecules transported depends on the nature, the concentration, and the fraction of the equivalent electrolysed of each of them; it is independent of the salts of the same acid which are not electrolysed.

M. A. W.

Chemical Reactions at Very High Temperatures. CONSTANTIN ZENGELIS (*Zeit. physikal. Chem.*, 1903, 46, 287—292).—The author shows that by the combustion of aluminium powder in a current of oxygen it is possible to reach temperatures comparable with that of the electric furnace. Thus he has been able to produce aluminium nitride and carbide, and to vaporise platinum, magnesia, and lime.

J. C. P.

Specific Heats of Aqueous Solutions. G. KALIKINSKY (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 1215—1238).—The author gives first of all an account of previous investigations on the specific heat of aqueous solutions, and then describes his own calculation, made with the view of discovering a connection between the molecular weight of a substance in solution and the specific heat of the solution.

The specific heat of a solution of x parts by weight of a substance in 100 of water may be expressed by the formula:

$$y = 1 - x/(100 + x) + c.x/(100 + x) \mp z.x/(100 + x),$$

where the specific of heat of water is taken as 1, and that of

the dissolved substance in the solid state denoted by c , while z represents the magnitude by which the specific heat of the solution is changed (relatively to the mean specific heat) by dissolving 1 gram of the substance in a given quantity of water. When the specific heat of a solution is less than that calculated from the specific heats of its constituent parts, which is the case for the strong mineral acids and bases and their salts, the negative sign in the formula must be taken. The value of z depends on the concentration of the solution and on the nature of the dissolved substance, and may be expressed by the formula: $z = a - \beta.x/(100 + x)$. From the known data for solutions of a number of electrolytes, the values of a and β have been calculated, and also the values of ae (e being the equivalent weight of the substance dissolved), which expresses the diminution of the specific heat of water containing in solution the equivalent weight of any substance; tables are also given containing the observed values of the specific heats of solutions of various concentrations, together with those calculated from the above formula. The values of ae for potassium chloride, bromide, nitrate, sulphate, chromate, and carbonate, sodium chloride, nitrate, sulphate, and carbonate, strontium chloride, barium chloride, magnesium chloride and sulphate, and manganese chloride are all either exactly or very nearly 38; for calcium chloride, 37; for potassium iodide, sodium bromide or iodide, nitric acid, and ammonium sulphate, 36; for ammonium chloride, 34; for strontium nitrate and nickel sulphate, 33; for copper sulphate, 32; for ammonium nitrate, 31; for lead nitrate, taking e as the molecular weight, 38; and for sulphuric acid, taking e as the molecular weight, 22. By substituting the value of z in the above formula, it is seen that β is the coefficient of the term $[x/(100 + x)]^2$, which is very small, so that in general it may be taken that $ez = ae = 38$; equivalent quantities of electrolytes in high degrees of dilution hence diminish the specific heat of the water in which they are dissolved by a constant amount. The values of β also show certain regularities, and for a series of similar compounds, such as KCl , KBr , and KI or $CaCl_2$, $SrCl_2$ and $BaCl_2$, it seems probable that β has the value B/e^2 , where B is a constant.

From the results given, it is also seen that for one and the same salt in different concentrations, the value of ez increases with the dilution.

The other substances investigated are the following: (1) Sucrose. In this case, $c = 0.301$ and z is practically constant and equal to 0.128, so that the specific heat of the solutions is expressed by $y = 1 - 0.571.x/(100 + x)$. (2) Tartaric acid; $c = 0.288$ and z is nearly constant, and = 0.090, so that $y = 1 - 0.622.x/(100 + x)$. (3) Acetic acid; $c = 0.4932$ and z diminishes, though but slightly, on dilution; $y = 1 - 0.37.x/(100 + x)$.

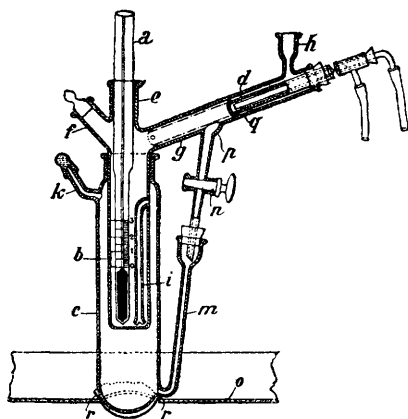
T. H. P.

Sublimation Lines of Binary Mixtures. W. BAKHUIS ROOZEBOOM (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 408—410. Compare Abstr., 1902, ii, 490; 1903, ii, 135).—From the consideration of the p , t , x -representation of the equilibria, for solid, liquid, and gaseous phases of binary mixtures, it may be deduced in what manner the

evaporation of the mixtures of two solid substances, or, inversely, their condensation on cooling a mixture of vapours, takes place at a constant pressure by a change of temperature. A. McK.

Distillation. EUGÈNE CHARABOT and JACQUES ROCHEROLLES (*Compt. rend.*, 1904, 138, 497—499).—When two non-miscible liquids are distilled by passing the vapour of the more volatile into the less volatile liquid, two cases arise, according as the temperature of the latter liquid is lower or higher than that at which the two liquids would simultaneously boil if heated in the same vessel. In the first case, the vapour of the more volatile would condense in the less volatile liquid and form two liquid layers, a case already considered (compare Abstr., 1902, ii, 552); whilst in the second case no such condensation would occur, the distillation process would be continuous, and the ratio of the weight of the less volatile to that of the more volatile liquid in the distillate is given by the formula $P/P' = M\phi/M'h$, where M and M' are the molecular weights of the two substances, ϕ the vapour pressure of the less volatile liquid at the temperature of the mixed vapours, and h the pressure in the apparatus; the ratio P/P' can be increased (1) by increasing the temperature of the less volatile liquid, or (2) by decreasing the pressure in the apparatus. Experimental values for P/P' obtained with water and oil of turpentine agree closely with those calculated from the ratio $M\phi/M'h$. M. A. W.

Modification of Beckmann's New Boiling Apparatus for Heating in a Current of Vapour. GUSTAV WALTHER (*Ber.*, 1904, 37, 78—82).—The apparatus shown in the cut has the advantage over



Beckmann's new form (Abstr., 1902, ii, 303) that the parts are detachable; hence it is less liable to fracture and can be constructed more cheaply. The parts are made air-tight during an experiment by the insertion of thin sheets of asbestos paper. The solvent is boiled in the jacket, c , the vapour passing through i into the boiling tube, b , and subsequently into the arm, g , where it is condensed; at first the movable condenser, d , is in its lowest position (dotted), so that the condensed liquid runs back into b . To observe the boiling point

and volume, the burner is removed, k opened to equalise the pressure, and the thermometer raised completely out of the liquid and its volume read; then the thermometer is put into its original position, k closed, the liquid again boiled, and the boiling point observed when constant. As long as the condenser is in its lowest position, liquid

accumulates in *b*; by raising it, the condensed liquid passes back through *n* into the vapour jacket. As long as *n* is open, the burner may be removed without causing the liquid in *b* to flow over into *c*, as the tube *h* is open to the air.

W. A. D.

Freezing Point and Boiling Point Experiments in Connection with Molecular Weight Determinations. ERNST BECKMANN (*Zeit. physikal. Chem.*, 1903, 46, 853—866).—It has been found, even after special purification of the material and with the most accurate work, that methylene iodide has two freezing points, $4\cdot0^{\circ}$ and $4\cdot7^{\circ}$. It therefore appears that methylene iodide crystallises in two forms, and the author, using solutes of known molecular weight, finds the mean depression constant for the more stable form (m. p. $4\cdot7^{\circ}$) to be 144, whilst that for the other is 137. The molecular weights of sulphur, selenium, phosphorus, and iodine in methylene iodide have been determined, and the values found point to the formulæ S_8 , Se_{10} , P_4 , I_2 (compare Beckmann, *Abstr.*, 1890, 447; Beckmann and Stock, *Abstr.*, 1895, ii, 382; Beckmann and Pfeiffer, *Abstr.*, 1897, ii, 363; Garelli and Bassani, *Abstr.*, 1901, ii, 541).

The molecular weight of aluminium bromide in bromine determined by the boiling point method is that required by the formula Al_2Br_6 . The bromide was prepared directly in the boiling tube, and the value of the elevation constant taken was 52° (arrived at by using tetra-bromomethane as solute). Further experiments with stannic bromide, antimony pentabromide, and arsenic tribromide in boiling bromine pointed to the respective formulæ $SnBr_4$, $SbBr_5$, and $AsBr_3$.

J. C. P.

Variation of the Melting Point of Glauber's Salt with Pressure. GUSTAV TAMMANN (*Zeit. physikal. Chem.*, 1903, 46, 818—826).—By finding the temperatures corresponding with certain applied pressures, the author has determined the fusion curve for Glauber's salt. At low pressures, this substance expands on melting, whilst at high pressures it contracts. In accordance with this, the fusion curve exhibits a maximum which is found to be about the pressure 750 kilograms per square centimetre, and a temperature about $0\cdot25^{\circ}$ above the ordinary point of fusion of Glauber's salt. There is reason to suppose that the fusion curves of all substances would exhibit maxima if the applied pressures were high enough; the special feature of the fusion curve for Glauber's salt is that the maximum is reached at a comparatively low pressure. The fusion curve, obtained as described, lies above that previously deduced from the volume alterations accompanying fusion.

J. C. P.

Molecular Lowering of the Freezing Point of Water Produced by Concentrated Solutions of Certain Electrolytes. HARRY C. JONES and FREDERICK H. GETMAN (*Zeit. physikal. Chem.*, 1903, 46, 244—286).—An extension of previous work (see Jones and Chambers, *Abstr.*, 1900, ii, 262; Chambers and Frazer, *ibid.*, ii, 526). An outline of some of the experiments described in detail in this paper has already been published (*Abstr.*, 1902, ii, 489). The

electrolytes for which a minimum value of the molecular depression has been found include lithium, ammonium, sodium and potassium chlorides, lithium nitrate, potassium carbonate, phosphoric acid, and sodium hydroxide. No minimum has been found for ammonium nitrate, potassium dihydrogen phosphate, ammonium, sodium, and potassium sulphates, and sodium carbonate; except, however, in the case of ammonium nitrate, it was not possible to examine these salts in very concentrated solution. If the molecular depressions are plotted against the concentrations as abscissæ, the curve for an acid lies in general above the curves for its alkali salts. The molecular boiling point elevation exhibits a similar minimum in many cases, but at higher concentration than the minimum observed for the freezing point depression of the same salt.

There is no evidence of irregularity in the conductivity-concentration curves at the position of the minimum molecular depression, and the refractivity of the solutions, which has been examined in a number of cases, is also perfectly regular. The most satisfactory interpretation of the phenomena referred to is that given by Jones and Chambers (*loc. cit.*). J. C. P.

Cryoscopic Behaviour of Halogen Compounds of the Elements when Dissolved in Phosphorus Oxychloride. GIUSEPPE ODDO and MARIO TEALDI (*Gazzetta*, 1903, 33, ii, 427—449. Compare Abstr., 1901, ii, 492).—A systematic study of the cryoscopic behaviour of the halogen salts of all the more common elements when dissolved in phosphorus oxychloride. The following halogen salts are insoluble in the solvent: the chlorides of lithium, sodium, potassium, copper, silver, calcium, strontium, barium, zinc, cadmium, cobalt, nickel, selenium, tellurium, chromium, and uranium; the bromides of lithium, sodium, potassium, selenium, tellurium, and cadmium; and cadmium and tellurium iodides. The alkaline iodides are decomposed to some extent, iodine being liberated. Some of the salts form compounds with the solvents; these are: $\text{SbCl}_5, \text{POCl}_3$; $2\text{SnCl}_4, \text{POCl}_3$; $\text{AlCl}_3, \text{POCl}_3$; $\text{BBr}_3, \text{POCl}_3$; $2\text{MgCl}_2, \text{POCl}_3$. The lower haloids of these elements, which form two halogen derivatives, give, as a rule, normal values for the molecular weight; for example, phosphorus trichloride and tribromide, arsenic trifluoride and tribromide, sulphur chloride and bromide, and iodine chloride. But the higher halogenated compound always undergoes, to a greater or less extent, dissociation into two parts; this behaviour is shown by phosphorus pentachloride and pentabromide, bismuth trichloride and tribromide, sulphur tetrachloride, SnCl_4 , platinum tetrachloride, ferric chloride, and auric chloride. In some cases, for example, phosphorus pentachloride and pentabromide, bismuth tribromide, and auric chloride, the dissociation into two parts is complete. With the exception of phosphorus pentabromide, all the substances giving abnormal values with phosphorus oxychloride have, in benzene solution, a normal molecular value. It is contended that in phosphorus oxychloride solutions complex ions exist, such, for example, as: PCl_4^+ , chlorophosphonium; B_2Cl_2^+ , chlorobismuthonium; PtCl_3^+ , chloriplatinum. The

solutions of PCl_5 and PBr_5 in phosphorus oxychloride are colourless, and therefore do not contain free halogen; this is particularly striking, because in benzene solutions the pentabromide is completely resolved into tribromide and free bromine, which imparts a brown colour to the solution.

Silicon tetrachloride and tetrabromide give normal values for the molecular weight in phosphorus oxychloride. W. A. D.

Molecular Rise of the Critical Temperature. JACOBUS H. VAN'T HOFF (*Chem. Centr.*, 1904, i, 422—423; from *Chem. Weekblad.*, 1, 93—96).—The original paper contains a theoretical discussion of the fact observed by Centnerszwer (this vol., ii, 158) that when molecular quantities of non-volatile substances are dissolved in liquid ammonia or sulphur dioxide, the critical temperature is raised by about the same amount in each case. The molecular rise of the critical temperature was found to be 724 for liquid sulphur dioxide, and 219 for ammonia. It is shown that considerations based on the osmotic pressure of the dissolved substance lead to the conclusion that the relative molecular rise of the critical temperature is proportional to the molecular weight of the solvent. According to Deprez and Trouton's rule, the law of the molecular rise of the boiling point must obtain more exactly for coincident temperatures than for the boiling points themselves.

E. W. W.

Theory of the Critical State. Difference between Gasogenic and Liquidogenic Substances. ISIDOR TRAUBE (*Zeit. anorg. Chem.*, 1904, 38, 399—409. Compare Abstr., 1902, ii, 551; this vol., ii, 110).—A further exposition of the author's theory as to the discontinuity of the gaseous and liquid state at the critical temperature. Further experiments are described in support of the views expressed.

A. McK.

Duhem's "Regnault Law." JAN VON ZAWIDZKI (*Zeit. physikal. Chem.*, 1903, 46, 21—29).—The extension of the "Regnault Law" to homogeneous binary liquid systems has led Duhem to propose for these a fifth general type of vapour pressure curve. The experimental evidence for this type is examined by the author and found to be quite inadequate. He shows that in the system ether—water, the three-phase and two-phase pressures (compare Kuenen and Robson, Abstr., 1899, ii, 356) are in general different from the vapour pressure of pure ether. He shows also that, contrary to the observations of Holley (Abstr., 1902, ii, 443), vapour pressure curves for mixtures of propyl alcohol and amyl iodide exhibit maxima.

J. C. P.

Vapour Pressure of Solid Solutions. ALEXANDER W. SPERANSKI (*Zeit. physikal. Chem.*, 1903, 46, 70—78).—The author describes a modified form of the Bremer-Frowein tensimeter, with which he has determined the vapour pressure of solid solutions of β -naphthol in naphthalene at various temperatures from 60° to 85°. The higher the percentage of β -naphthol the lower is the

vapour pressure of the solid solution, and the author, applying the rules that are valid for liquid solutions, has calculated the molecular weight of β -naphthol from the lowering of the vapour pressure, the very slight tension of the β -naphthol itself being negligible. The values of the molecular weight found are, for example, 198 for a solution containing 14.6 molecular per cent. of β -naphthol, and 255 for one containing 33.6 molecular per cent. These values lie between the single and double molecular weight of β -naphthol (compare Küster, Abstr., 1895, ii, 439). J. C. P.

Pressure and Composition of the Vapours of Solutions in Aqueous Alcohol. IWAN A. KABLUKOFF, A. SOLOMONOFF, and A. GALINE (*Zeit. physikal. Chem.*, 1903, 46, 399—407. Compare Kablukoff, Abstr., 1893, ii, 154; Wrewsky, Abstr., 1901, ii, 56).—The effect of dissolving sodium and potassium chlorides, bromides, and iodides, and dextrose in aqueous alcohol containing from 10—46 per cent. of alcohol is to increase the vapour pressure of the aqueous alcohol. The increase varies with the nature of the dissolved salt, but for a given salt is approximately proportional to the concentration of the latter. There is apparently a connection between the increase of vapour pressure produced by the salts and their solubility in alcohol and water. Thus, at 47.5°, the molecular increase of vapour pressure produced by sodium chloride is equal to that produced by potassium chloride, and lies between 8 and 13 mm. of mercury, according to the concentration of the alcohol. Salts which are notably more soluble in alcohol than these chlorides as, for example, potassium bromide and iodide, cause a smaller molecular increase of vapour pressure. Tartaric acid, which is very soluble both in water and in alcohol, scarcely affects the vapour pressure of aqueous alcohol, whilst mercuric chloride, which is more soluble in alcohol than in water, actually lowers the vapour pressure.

The change of vapour pressure produced by electrolytes is greater than that produced by non-electrolytes, for dextrose (the solubility of which in alcohol is comparable with that of sodium and potassium chlorides) gives a molecular increase of vapour pressure of about 6 mm.

When sodium chloride, potassium chloride, bromide and iodide are dissolved in aqueous alcohol, the percentage of alcohol in the vapour is raised; when tartaric acid is the solute, the composition of the vapour is not affected; when mercuric chloride is the solute, the percentage of alcohol in the vapour falls. The extent by which the percentage of alcohol in the vapour is increased by the solution of sodium chloride, &c., is proportional to the salt concentration. The extent of the increase is the same for sodium and potassium chlorides, and rather less for potassium bromide and iodide.

These results are attributed to the effect of the dissolved substance on the alcohol-water complexes that are supposed to exist in aqueous alcohol. If the added salt has a strong affinity for the water molecules, it will tend to break up the alcohol-water complexes, and the alcohol molecules thus set free will go to increase the vapour pressure of the solution. J. C. P.

Advantage of Hydrogen as Unit of Comparison in Determining the Specific Gravity of Gases. ALEXANDER P. LIDOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 1245—1246).—The author's reasons for displacing air by hydrogen as a standard in gaseous specific gravity determinations are: (1) hydrogen has a much smaller sp. gr. than air, so that the differences between the sp. grs. of different gases are more striking than where air is taken as standard. (2) Air is not an element, but a complex mixture of gases, and investigations by the author show that the proportion of nitrogen in the inert portion of the air varies by as much as 8 per cent.

T. H. P.

New Gravimetric Method of Determining the Specific Gravity of Gases. ALEXANDER P. LIDOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 1239—1245).—The method here described for determining the sp. gr. of gases is based on the absorption of many gases by heated magnesium or manganese (this vol., ii, 250); the volume of gas absorbed is measured by ordinary gasometric apparatus, and the increase in weight of the absorbing metal is also determined. With cyanogen (manganese) and with atmospheric and chemical nitrogen, carbon dioxide, nitrous oxide, sulphur dioxide, and ammonia (magnesium) the method gives good results. A sketch of the apparatus used is given.

T. H. P.

Resistance of Glass Tubing to Bursting Pressure. WALTER P. BRADLEY and A. W. BROWNE (*J. Physical Chem.*, 1904, 8, 37—55).—The bursting pressure of a large number of samples of different kinds of glass was determined. As the bursting pressure is found in general to vary directly as the thickness of the wall and inversely as the bore, the values for PB/W were compared, where P is bursting pressure, B the bore, and W the thickness. The results show that Jena glass and soft glass have the highest values, Bohemian glass the lowest. Lead glass, besides possessing a high bursting pressure, is very trustworthy, the most erratic tube examined being only 15 per cent. below the normal strength. The strength of tubes depends greatly on their previous history, thus a sample once tested to about 100 atmospheres would not withstand as much again, but would probably burst at very low pressures.

L. M. J.

Viscosity of Solutions. JULIUS WAGNER [with JOHANNES MÜHLENBEIN] (*Zeit. physikal. Chem.*, 1903, 46, 867—877).—In comparing the viscosities of different metals in solutions of their salts, the author has previously (Abstr., 1890, 441) shown that for allied metals the viscosity decreases as the atomic weight increases. It is now shown, however, that the weights of water per litre of the normal solutions of chlorides, nitrates, or sulphates of the metals vary in a very similar manner, and it is therefore doubtful whether there is any direct relation between the viscosity of the metals and the periodic law.

Euler's explanation of negative viscosity is discounted by Mühlenbein's measurements, showing that in non-electrolytic cases

also the viscosity of the solvent may be lowered by the solute, even when the viscosity of the solute itself is higher than that of the solvent. Examples of this diminished viscosity are: cyanobenzene, nitromethane, and allylthiocarbimide in ethyl alcohol, nitrobenzene and cyanobenzene in *isobutyl* alcohol. The viscosity of solutions of the nitrotoluenes in ethyl alcohol varies with the concentration in a peculiar manner; with *o*-nitrotoluene, there is an inversion point; with *m*-nitrotoluene, there is a minimum, with *p*-nitrotoluene, a maximum. In the author's view, a solute diminishes the quantity of solvent in a given space, and this leads to a diminution of the viscosity, which diminution, however, may be partly or more than made good by the solute itself. According to the relative magnitude of the various factors, the viscosity of the solvent may be increased or diminished.

J. C. P.

Osmose. AUGUSTE PONSOT (*Compt. rend.*, 1904, 138, 356—358. Compare Guillemin, this vol., ii, 161).—A claim for priority (compare Abstr., 1896, ii, 411, 626; 1898, ii, 16, 471). From theoretical considerations, the author deduces the following relation: two solutions which at the same temperature have the same vapour pressure, or are in osmotic equilibrium, have the same osmotic pressure only when they are both under the same pressure *P*.

M. A. W.

Solubility and Diffusion in Solution of Dissociated Gases. OWEN W. RICHARDSON (*Phil. Mag.*, 1904, [vi], 7, 266—274).—A mathematical paper in which equations for solubility and rate of diffusion are deduced; the first is very simply obtained and is interesting, namely, $a^n/A = k_o/k_i$, where *n* is the number of similar products of dissociation, *a* and *A* are the respective solubilities, and *k_o*, *k_i* are the dissociation constants outside and inside the solution. An expression for the variation of solubility with temperature is obtained dependent solely on the difference of the heats of solution of the dissociated and undissociated gas. The expression for the diffusion becomes somewhat complicated, involving two terms, one of which is proportional to the pressure and the other to its *n*th root. L. M. J.

Theory of Capillarity and Colloidal Solutions. FREDERICK G. DONNAN (*Zeit. physikal. Chem.*, 1903, 46, 197—212. Compare Abstr., 1901, ii, 439).—From the point of view of the Laplace-Gauss theory of capillary forces, the physical possibility of negative interfacial tension is considered, and the results to which it would give rise under specified conditions. In certain cases, the theory points to the production of extremely fine-grained heterogeneous mixtures, such as actually occur in colloidal solutions. Such two-phase systems may be due to the interaction of capillary forces in the manner indicated in the paper.

J. C. P.

Capillarity Constants and Specific Weights of Salts at their Melting Points. Method for Capillary Solubility Determination. S. MOTYLEWSKI (*Zeit. anorg. Chem.*, 1904, 38, 410—418).—The capillarity constants of a number of fused salts have been determined by Traube's method. Determinations of the specific gravity of various

salts at their respective melting points were also made, and a table is quoted showing the value for γ , the capillarity constant, for α^2 , where $\alpha^2 = 2\gamma/d$ (d = density), for the molecular volume and for the molecular surface energy $\alpha(m/d)^{\frac{2}{3}}$ of the individual salts. Solubility determinations, made by the capillary method, showed that water at 15° dissolves 0.33 per cent. of normal heptyl alcohol and 0.087 per cent. of normal octyl alcohol.

A. McK.

Constitution of Solutions of Salts. RICHARD ABEGG and ST. LABENDZINSKI (*Zeit. Elektrochem.*, 1904, 10, 77—81).—The ratios of the concentrations of the simple metallic ions in the solutions are measured by means of the potential differences between the solutions and the metals. These numbers are compared with the total concentrations of the ions in the same solutions, calculated from the conductivity. The nitrates, sulphates, chlorides, and acetates of zinc, cadmium, nickel, cobalt, iron, lead, and copper are examined; all the salts form complex ions (the number of simple metallic ions is very much smaller than the total number calculated from the conductivity). The nitrates form very few complex ions, the chlorides, sulphates, and acetates form more in the order given. The addition of an alkali salt of the same anion increases the concentration of the complex ions, the effect increasing from nitrate to acetate. This points to the complex ions being anions. When a solution of the acetates of an alkali metal and a heavy metal is diluted, the complex anions break up so rapidly that the concentration of the simple metallic ions in the dilute solutions may be greater than that in the more concentrated solution. This is also the case with cadmium chloride. If the concentration of the anion is kept constant and the salt of the heavy metal diluted, the small concentration of the simple metallic ions is approximately proportional to the total concentration of the salt.

T. E.

Researches on the Solubility of Sparingly Soluble Salts. WILHELM BOTTGER (*Zeit. physikal. Chem.*, 1903, 46, 521—619).—The author has found the solubility of a large number of sparingly soluble salts by determining the conductivity of water (1) when pure, (2) after saturating with the salt under examination. From this increase in conductivity due to the dissolved salt, its solubility can be calculated (compare, for the use of this method, Holleman, *Abstr.*, 1893, ii, 519; Kohlrausch and Rose, *Abstr.*, 1894, ii, 7; Kohlrausch and Dolezalek, *Abstr.*, 1902, ii, 72; Kohlrausch, *Abstr.*, 1903, ii, 528). Full details are given of the apparatus used, of the precautions adopted, and of the method of calculation employed, but for these the original paper must be consulted.

The numbers in the following table give for the respective salts the weight in grams per litre of saturated solution at 20°:

| | Silver. | Thallium. | Lead. |
|----------------|-----------------------|-----------------------|-----------------------|
| Chloride | 1.53×10^{-3} | 3.26×10^{-2} | 9.61×10^{-1} |
| Bromide | 0.84×10^{-4} | 0.48×10^{-2} | 8.34×10^{-1} |
| Iodide | — | 0.64×10^{-1} | 0.47×10^{-1} |

| | Silver. | Thallium. | Lead. |
|----------------|-----------------------|------------------------|------------------------|
| Cyanide | 2.2×10^{-4} | — | — |
| Thiocyanate .. | 1.4×10^{-4} | 3.15×10^{-1} | 4.50×10^{-1} |
| Bromate | 1.59×10^{-4} | 3.46×10^{-1} | 13.37×10^{-1} |
| Iodate | 4.35×10^{-2} | 0.58×10^{-1} | 1.83×10^{-2} |
| Oxalate | 3.65×10^{-2} | 15.77×10^{-1} | 1.80×10^{-3} |
| Phosphate ... | 0.64×10^{-2} | — | 1.35×10^{-4} |
| Carbonate ... | — | — | 1.5×10^{-3} |
| Sulphate | — | — | $4.23 \times 10^{-}$ |
| Sulphide | — | 0.21×10^{-1} | — |
| Oxide | 2.14×10^{-2} | — | 1.71×10^{-2} |

The numbers given for lead carbonate and oxide are only approximate. The solubility of calcium sulphate also was determined in the same way and found to be 2.04—that is, grams of calcium sulphate per litre of saturated solution.

The influence of the size of the particles on the solubility of a substance could be detected, but was not greater than 1—2 per cent. in the cases where this factor was specially considered. J. C. P.

‘Frost Curves’ [‘Reifkurven’]. WILHELM MEYERHOFFER (*Zeit. physikal. Chem.*, 1903, 46, 379—398. Compare Duhem, Abstr., 1901, ii, 227).—The author extends Duhem’s theory of ‘dew curves’ (‘Taufkurven’) to the case of solid substances. The ‘frost curves’ represent the variation of pressure and composition of the vapour in equilibrium with a mixture of two solids. According as these remain uncombined, or form double salts or mixed crystals, various types of curve are obtained (compare Roozeboom, Abstr., 1901, ii, 151). J. C. P.

Crystallisation in Binary Systems. WILDER D. BANCROFT (*Zeit. physikal. Chem.*, 1903, 46, 87—88).—A graphical method is described whereby from the freezing point curve for a binary system it is possible to determine the nature and relative amounts of the phases formed in solidification, provided no solid solutions occur.

J. C. P.

Inclusion and Occlusion of Solvent by Crystals. THEODORE W. RICHARDS (*Zeit. physikal. Chem.*, 1903, 46, 189—196).—As shown by experiments with barium chloride, the amount of moisture mechanically held by a crystalline salt diminishes with pulverisation and subsequent exposure. When, however, the particles are very small, the surface adsorption becomes marked, and the author therefore holds that hydrated salts, in the case of which application of heat is not permissible, cannot be accurately weighed according to any usual procedure. In the case of anhydrous salts, the removal of the included moisture requires the disintegration of the cell walls by mechanical, thermal, or chemical processes. It is suggested that the impurities enclosed in natural minerals might often be used as a clue to the manner of their growth, and to the mechanism of geophysical processes. J. C. P.

Complexes of Two Colloids: (I) of the Same Electrical Sign; (II) of Opposite Electrical Sign. VICTOR HENRI, S. LALOU ANDRE MAYER, and G. STODEL (*Compt. rend. Soc. Biol.*, 1903, 55 1669—1671; 1671—1673).—A mixture of two colloids of the same electrical sign, one of which is easily, the other with difficulty, precipitated by electrolytes (for example, silver and starch), can be precipitated no more easily than the more stable of the two components. The stability of the complex increases at first more slowly than the quantity of stable colloid added, but after a certain point becomes very great. The quantity of a stable colloid that must be added to an unstable colloid to give a stable complex increases with the quantity of unstable colloid.

The addition of a certain quantity of a negative colloid (for example, ferric hydroxide) to a positive colloid (for example, silver) precipitates both substances. It is possible, however, to have too little or too much of the negative colloid, and to get no precipitation, so that there is a critical point for such a colloid complex. If to an unstable colloid gradually increasing quantities of a colloid of the opposite electrical sign are added, the stability of the complex first diminishes, reaches a minimum, and then increases. The minimum corresponds with the critical point just referred to. The properties of the complex are not the same on the two sides of this minimum. Where the positive colloid predominates, the complex is precipitable by acidic ions; where the negative colloid predominates, by metallic ions. So generally, in an electric field, the complex moves in the same direction as the predominant component.

J. C. P.

Changes produced in Colloids by Coagulation. JACQUES DUCLAUX (*Compt. rend.*, 1904, 138, 571—572).—When a solution of a colloid is coagulated, the precipitate which is formed usually contains a certain amount of one of the radicles of the salt used to produce coagulation. It is shown that this change in the composition of the colloid is brought about by simple substitution of one of its radicles for an equivalent amount of one of the constituents of the salt. The solution, after coagulation, will contain a small amount of the radicle displaced from the colloid; the author proposes to make use of this fact in the investigation of the composition of complex organic colloids.

S. S.

Chemical Equilibrium. LEO PISSARJEWSKY (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 1204—1215).—The author has studied the reaction between silver and ferrous sulphates, and from the results obtained draws the following conclusions: (1) the reaction between Ag_2SO_4 and FeSO_4 reaches a state of equilibrium after 168 hours; the initial high velocity of the reaction diminishes extremely rapidly during the first 50 hours. (2) The constant of the equilibrium $\text{Ag}^+ + \text{Fe}^{++} \rightleftharpoons \text{Ag} + \text{Fe}^{+++}$ at 25° equals 0.00792 and the diminution of free energy +2870 cal. (3) The heating effect of the reaction (diminution of total energy) is +8683 cal. (4) Calculating by means of van't Hoff's formula, the constant becomes 1, and the diminution of free energy zero, at -48.7° . (5) If the reaction takes place in normal sodium sulphate solution, the constant

at 25° is 0.00326 and the diminution of free energy +3397 cal. (6) The determination of the constant is only possible at temperatures below 35° , because at that temperature basic iron salts separate from the solution, and these exert an influence on the magnitude of the constant.

T. H. P.

Densities of Fused Salts and the Chemical Equilibrium of their Mixtures. ERICH BRUNNER (*Zeit. anorg. Chem.*, 1904, **38**, 350—375).—Ostwald has endeavoured to determine equilibria of reciprocal salt pairs by calorimetric methods. The author endeavours to solve the same problem by volumetric methods.

Various salts were fused in an electric furnace and the densities of the fused masses determined. The following values were obtained: potassium chloride, $1.450 - 0.00057 (t - 900)$; potassium bromide, $1.991 - 0.00080 (t - 900)$; potassium carbonate, $1.900 - 0.00046 (t - 900)$; potassium sulphate, $1.96 - 0.0005 (t - 900)$; sodium chloride, $1.500 - 0.00054 (t - 900)$; sodium bromide, $2.2125 - 0.00080 (t - 900)$; sodium carbonate, $1.9445 - 0.00040 (t - 900)$; sodium sulphate, $2.065 - 0.00045 (t - 900)$; lithium chloride, $1.375 - 0.00043 (t - 900)$; lithium bromide, $2.30 - 0.0007 (t - 900)$; lithium carbonate, $1.765 - 0.00034 (t - 900)$; lithium sulphate, $1.981 - 0.00039 (t - 900)$.

The density of fused sodium chloride was controlled by a dilatometric method, but the value obtained for potassium bromide was abnormal.

The following conditions of equilibria were determined: At 900° , 52 per cent. of $(\text{KCl} + \frac{1}{2}\text{Na}_2\text{CO}_3) \rightleftharpoons$ 48 per cent. of $(\text{NaCl} + \frac{1}{2}\text{K}_2\text{CO}_3)$, 63 per cent. of $(\text{KCl} + \frac{1}{2}\text{Li}_2\text{CO}_3) \rightleftharpoons$ 37 per cent. of $(\text{LiCl} + \frac{1}{2}\text{K}_2\text{CO}_3)$, 53 per cent. of $(\text{KBr} + \frac{1}{2}\text{Na}_2\text{CO}_3) \rightleftharpoons$ 47 per cent. of $(\text{NaBr} + \frac{1}{2}\text{K}_2\text{CO}_3)$, 56 per cent. of $(\text{NaCl} + \frac{1}{2}\text{Li}_2\text{CO}_3) \rightleftharpoons$ 44 per cent. of $(\text{LiCl} + \frac{1}{2}\text{Na}_2\text{CO}_3)$, 60 per cent. of $(\text{NaCl} + \frac{1}{2}\text{Li}_2\text{SO}_4) \rightleftharpoons$ 40 per cent. of $(\text{LiCl} + \frac{1}{2}\text{Na}_2\text{SO}_4)$.

A. McK.

The Conditions of the Indifferent State. E. ARIÈS (*Compt. rend.*, 1904, **138**, 416—419).—It is shown from theoretical considerations that the indifferent point can be attained whatever be the number of phases in the system. This is proved in three cases: (1) when the number of phases exceeds the number of constituents in the system by units, (2) when the number of phases and constituents are equal, (3) when the number of phases is less than that of the constituents by units.

S. S.

Classification and Theory of Coupled Oxidation and Reduction Processes. ROBERT LUTHER and NIKOLAI SCHILOFF (*Zeit. physikal. Chem.*, 1903, **46**, 777—817. Compare Schiloff, *Abstr.*, 1903, ii, 276).—The processes considered are those in which three substances, *A*, *B* and *C*, take part, the discussion being further limited by the condition that whilst *A* and *B* react readily, *A* and *C* hardly react at all, except when *B* is present. In such cases, *A* is to be regarded as actor, *B* as inductor, and *C* as acceptor (see Schiloff, *loc. cit.*). Two possible explanations of such coupled reactions are suggested: (1) the reaction between actor and acceptor may be catalytically accelerated

by the inductor, which, however, is at the same time being gradually transformed by the actor into a catalytically inactive substance: in short, a catalytic action during which the catalytic agent is itself being removed. (2) The inductor may form with the actor or acceptor or with both an intermediate product, the action of which results in the change of all three original substances. Which of these two explanations is to be adopted in a particular case will have to be deduced from the way in which the induction factor (see Schiloff, *loc. cit.*) varies with the concentration of the reacting substances.

A systematic variation of the reacting substances themselves will show which of them plays a specific part in the reaction, and a classification of coupled reactions may be made according as the term "specific" has to be applied to one or to two of the three reacting substances. I. Where only one is specific, that one may be (a) the inductor, (b) the actor, (c) the acceptor. Examples of (a) are found in the numerous reactions where a ferrous salt acts as inductor (compare Manchot, *Abstr.*, 1900, ii, 546; 1901, ii, 549; 1903, ii, 151, 152). In such reactions, the inductor itself forms an intermediate product and must therefore be a substance capable of several stages of oxidation. With the same inductor, the chemical character of the actor and acceptor may be varied within wide limits. Examples of (b) are the cases where bromic acid is the actor (see Schiloff, *loc. cit.*). No example of (c) is known. II. Where two of the reacting substances are to be regarded as specific and form complexes, these two may be (a) acceptor and inductor, (b) actor and acceptor, or actor and inductor. An example of (a) is found in the reaction between chromic or permanganic acid (actor), arsenious acid (inductor), and tartaric acid (acceptor) (Schiloff, *loc. cit.*), or in that between permanganic acid, ferrous oxide, and chlorine ions (Wagner, *Abstr.*, 1899, ii, 275). In case (b) the intermediate complex must be a combination of oxidising and reducing agents. Cases of the intensification of oxygen ('Sauerstoffactivierung') come under this head.

J. C. P.

Heterogeneous Catalytic Reactions. I. Catalysis of Oxygen-hydrogen Gas by Platinum. MAX BODENSTEIN (*Zeit. physikal. Chem.*, 1903, 46, 725—776. Compare *Abstr.*, 1899, ii, 733).—The catalytic combination of oxygen and hydrogen in presence of compact platinum proceeds rapidly at the ordinary temperature, and the velocity of combination has been determined by measuring at intervals the pressure of the system at constant volume; the decrease of pressure observed is a measure of the water vapour formed.

When the platinum has the same temperature as the surrounding gas, a film of water is deposited on its surface. In these circumstances, the reaction is found to be approximately of the first order, the velocity coefficient increasing slightly with the time when the gases are mixed in equivalent proportion or when the hydrogen is in excess, but decreasing with the time when the oxygen is in excess. The temperature coefficient of the velocity is very much smaller than is usual in chemical reactions, and this observation bears out the view that what is actually measured is the velocity of a physical process, in fact, the rate of solution of oxygen (or of hydrogen, when the gas

contains excess of oxygen) in the film of water deposited on the platinum, the actual combination of the gases at or in the platinum taking place with a nearly infinite velocity (compare Ernst, Abstr., 1901, ii, 495).

When the surface of the platinum is kept dry by making it warmer than its surroundings, the rate of combination is much greater than in the previous case, but does not conform even approximately to the course of a unimolecular reaction. The increase of the velocity coefficient calculated for a unimolecular reaction amounts to 100 per cent. or over for nine-tenths of the total possible change, and this is the case whether hydrogen or oxygen is in excess. As in the experiments with moist platinum, the temperature coefficient of the velocity is very small, and the view is adopted that what is actually measured is the rate of absorption of oxygen by the platinum, the subsequent combination of the gases in the platinum being a very rapid process. That the course of the change deviates so much from that of a unimolecular reaction is probably due to the disturbance caused by currents of water vapour escaping from the platinum; this would explain the lower values of the velocity coefficient, obtained in the earlier stages of the reaction, when the quantity of escaping water vapour is specially large. In harmony with this explanation, it has been found that the rate of action, which is but slightly affected by altering concentration or temperature, may be diminished by a "poison," such as iodine, and that the course of combination then approaches more and more to that of a unimolecular reaction.

These experiments, therefore, throw no light on the real nature of the catalytic acceleration due to platinum, for the actual combination of oxygen and hydrogen thus induced proceeds with too high a velocity to be susceptible of accurate quantitative measurement.

J. C. P.

Decomposition of Antimony Hydride as an Example of a Heterogeneous Catalytic Reaction. ALFRED STOCK and OSKAR GUTTMANN (*Ber.*, 1904, 37, 901—915).—The curve representing the relationship between the percentage of gaseous antimony hydride decomposed and the time varies considerably with the surface of the glass vessel in which the gas is kept. With a clean, smooth surface, the curve has an S-shape; a vessel, the inner surface of which had been etched with hydrofluoric acid, gave a curve slightly S-shaped, and a vessel coated with antimony, first by warming and then at the ordinary temperature, gave a curve of hyperbolic form. The deposited antimony accelerates the decomposition, but the deposit loses this property to a considerable extent after some time. Microscopic study has shown that the different effects obtained with antimony deposited in the cold and at higher temperatures correspond with differences in the physical states (for example, the crystalline nature) of the deposits.

Van't Hoff's equation, $K = 1/t \cdot \log P_0 / (3P_0 - 2P_t)$ does not hold good. Better concordance is obtained by using the equation

$$V = 2(x_1 - x_2) / (x_1 + x_2)(t_2 - t_1),$$

where V is the amount of hydride decomposed in unit time (1 hour)

calculated on the mean of the amounts present at the beginning and end of the time. In calculating x , attention must be paid to the fact that the hydride does not closely follow Boyle's law on account of the considerable molecular attraction; at 15° and 760 mm. the deviation amounts to 16 mm. This is allowed for in the tables given.

It is considered probable that the reaction takes place at the surface of the antimony instantaneously and that what is measured are the diffusion phenomena. Bodenstein's views (preceding abstract) are supported. J. J. S.

Influence of Persulphates on the Catalytic Decomposition of Hydrogen Peroxide by means of Colloidal Platinum. T. SLATER PRICE and A. D. DENNING (*Zeit. physikal. Chem.*, 1903, 46, 89—102).—The decomposition of hydrogen peroxide by colloidal platinum is accelerated by adding potassium persulphate, and the acceleration is probably proportional to the amount of persulphate added. The effect of the persulphate is mainly catalytic, for it undergoes only slight decomposition itself. The decomposition of hydrogen peroxide is accelerated also by free persulphuric acid, but the latter is itself decomposed, probably by interaction with the hydrogen peroxide, thus: $\text{H}_2\text{O}_2 + \text{H}_2\text{S}_2\text{O}_8 = 2\text{H}_2\text{SO}_4 + \text{O}_2$. J. C. P.

Catalytic Oxidation of Organic Substances with Concentrated Sulphuric Acid. I. Chemical Kinetics of the Kjeldahl Analysis and of the Naphthalene Oxidation Process. GEORG BREDIG and JOHN WESLEY BROWN (*Zeit. physikal. Chem.*, 1903, 46, 502—520).—The authors have followed the gradual oxidation of aniline sulphate and naphthalene in hot concentrated sulphuric acid (with and without catalytic accelerators) by determining at intervals the amount of gas evolved from the reaction mixture. With a thermo-regulator, the temperature of the paraffin bath used could be kept constant within 0.5° , and it was shown that the courses of parallel experiments with the same amount of reagents were coincident. Analysis of the gases evolved in the oxidation of aniline showed that the ratio CO_2/SO_2 (by weight) was 0.31, whilst according to the equation, $(\text{C}_6\text{H}_5\text{NH}_2)_2\text{H}_2\text{SO}_4 + 28\text{H}_2\text{SO}_4 = (\text{NH}_4)_2\text{SO}_4 + 28\text{SO}_2 + 12\text{CO}_2 + 32\text{H}_2\text{O}$, it should be 0.29. On the assumption that the oxidation of naphthalene goes only as far as phthalic acid, thus: $\text{C}_{10}\text{H}_8 + 9\text{H}_2\text{SO}_4 = \text{C}_6\text{H}_4(\text{CO}_2\text{H})_2 + 9\text{SO}_2 + 2\text{CO}_2 + 10\text{H}_2\text{O}$, the ratio CO_2/SO_2 (by volume) should be 0.22, whilst analysis gave values between 0.15 and 0.19.

Both reactions are subject to disturbing elements, but are approximately of the first order, and the influence of catalytic agents, notably mercury and copper sulphates, is very evident in the values of the constants obtained. The accelerating influence of these catalysts is nearly proportional to their concentration. Copper is, relatively to mercury, less effective in the oxidation of naphthalene than in the oxidation of aniline. The accelerating effect of copper and mercury together is greater than the sum of their separate effects. The presence of small quantities of water does not appreciably affect the velocity of oxidation. Potassium sulphate and phosphoric oxide do not

act in either oxidation as catalytic agents, but merely make it possible to work at higher temperatures. The temperature-coefficient of the reaction velocity between 200° and 300° (with or without catalysts) is of the same magnitude as in other reactions. J. C. P.

Decomposition-tension of Salts and their Anti-fermentative Properties. HUGH McGUIGAN (*Amer. J. Physiol.*, 1904, 10, 444—451).—The minimum amount of salts, bases, and acids required to inhibit the action of malt diastase was determined. In different salts of the same acids, the inhibitory power varies inversely with the solution tension of the cathion. The action of the cathion appears to be determined by the ease with which it gives up its positive charge. In different salts of the same metal, the power varies inversely with the solution-tension of the anions. The inhibitory power of the cathions is also inversely proportional to the heat of ionisation; that of any salt is inversely proportional to the sum of the solution-tensions of its ions, or to the decomposition tension of the salt. W. D. H.

Shaking and Stirring Apparatus. JULIUS W. BRUHL (*Ber.*, 1904, 37, 918—924).—A stirrer is described which can be used for flasks fitted with reflux condensers, a paraffin oil or mercury trap being employed.

The shaking apparatus consists of a flat tambourine shaped brass case fixed eccentrically to a grooved wooden disc, which is driven by a small motor. A movable brass ring is fixed around the periphery of the brass tambourine, and to this ring the vessels to be shaken are attached by means of metallic rings. The vessels attached to these rings by the aid of cord may be fitted with reflux condensers and even dropping funnels. The apparatus is of great use in the preparation of organo-magnesium compounds. J. J. S.

Inorganic Chemistry.

Action of Ozone on Hydrogen. GEORGE PICKEL (*Zeit. anorg. Chem.*, 1904, 38, 307—310).—Ozone acts on hydrogen at temperatures below 100° , and the union of the active oxygen with hydrogen takes place with greater rapidity than the transformation into ordinary oxygen.

Sulphuric acid of sp. gr. 1.18 was electrolysed with a current of about 0.9 ampere and 3—7 volts, the electrodes being made of lead. The gaseous mixture was then dried and passed into a paraffin or air-bath, regulated at the desired temperature, and the quantity of water formed was weighed. The experiments were conducted mainly at temperatures above 150° . In some experiments, the ozone was estimated by titration with potassium iodide. A. McK.

Limits of Stability of Hydrogen Peroxide. WALTHER NERNST (*Zeit. physikal. Chem.*, 1903, 46, 720—724).—Hydrogen peroxide is an endothermic compound, and therefore its equilibrium concentration in the reaction $2\text{H}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{O}_2$ should increase as the temperature rises. From the formula $q = RT^2(d\log K)/dT$, the author estimates as follows the amount of hydrogen peroxide which at certain given temperatures should coexist with water vapour and oxygen at a pressure of 0.1 atmosphere.

| | | | | | |
|--|-------|-------|-------|--------|----------|
| T | 2784° | 2154° | 1493° | 1140° | 923° |
| Per cent. H_2O_2 | 0.66 | 0.24 | 0.028 | 0.0032 | 0.00036 |
| | | | | | J. C. P. |

Generator for the Continuous Preparation of Gases on a Large Scale in the Laboratory. RESTON STEVENSON and W. MCKIM MARRIOTTE (*J. Amer. Chem. Soc.*, 1904, 26, 64—66).—A method is described for producing a continuous evolution of hydrogen chloride by the contact of streams of hot strong sulphuric acid and concentrated hydrochloric acid in a glass tower filled with glass beads. For details of the apparatus, the description and diagram in the original must be consulted. E. G.

Electrolysis of Chloric Acid and Chlorates. ANDRÉ BROCHET (*Compt. rend.*, 1904, 138, 200—203. Compare Abstr., 1903, ii, 210, 352).—When a solution of barium, sodium or copper chlorate is electrolysed with a copper anode, the quantity of copper that dissolves is greater than that deposited on the cathode of a voltameter; this is due to the fact that part of the copper enters into solution in the form of a cuprous salt which is subsequently oxidised. The formation of the cuprous salt was detected by an examination of (1) the action of chloric acid and copper chloride on copper, (2) their behaviour on electrolysis with a copper anode. The cuprous salts formed are decomposed by the copper chlorate or chloric acid present with the formation of cupric chloride and hydroxide; the latter in an acid medium passes into solution, and in the case of a copper chlorate solution forms the basic salt, $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$, in which the Cl_2 is in part replaced by ClO_2 . In the case of an alkali chlorate or alkali earth chlorate solution, the base formed at the cathode partly decomposes the basic salt, the oxide so produced being partly reduced by the hydrogen produced at the cathode. M. A. W.

Electrolytic Formation of Periodic Acid and its Salts. ERICH MÜLLER (*Zeit. Elektrochem.*, 1904, 10, 49—68).—Potassium periodate can be prepared electrolytically without the use of a porous diaphragm by electrolysing a saturated solution of potassium iodate in normal potassium hydroxide containing 0.1 per cent. of potassium chromate with a current density of 0.05 ampere per sq. cm. at the platinum foil anode and a platinum wire cathode. The investigation published with Friedberger (Abstr., 1902, ii, 556) is continued, with the following results. The fact that much better yields of periodate are obtained at platinum cathodes in alkaline solutions than in

neutral or acid solutions is probably due to the higher values of the anodic polarisation of platinum in alkaline solutions. The diminished yields at higher temperatures are ascribed to smaller anodic polarisation. Increase of yield as the electrolysis is prolonged goes along with a rise of anodic polarisation. The good yields at a lead peroxide anode cannot be ascribed to a large value of the anodic polarisation (which is about the same as that found with platinum); they are probably due to a catalytic acceleration of the oxidation.

At platinum anodes, no periodate is formed from a neutral solution of potassium iodate; in presence of Cl , SO_4 or ClO_3 ions, however, periodate is formed. Whether this is due to intermediate formation of hypochlorite, persulphate, or chlorous acid or to some catalytic action is left undecided. T. E.

Sulphur Bromide. GEORG KORNDÖRFER (*Arch. Pharm.*, 1904, 242, 156—160).—In the preparation of hydrogen bromide by passing hydrogen sulphide into 30 c.c. of bromine covered with water to a depth of 2 cm., the vessel being cooled with water, a few c.c. of a heavy, red, oily liquid were obtained; this contained 69.0 per cent. of bromine; S_2Br_2 requires 71.4.

It is decomposed slowly by cold water, rapidly by hot. Its decomposition by potash was found to take place very nearly according to the equation $2\text{S}_2\text{Br}_2 + 6\text{KOH} = 4\text{KBr} + \text{K}_2\text{SO}_3 + 3\text{S} + 3\text{H}_2\text{O}$; a weighed quantity was mixed with excess of *N*-alkali hydroxide solution, and the excess titrated finally with *N*-acid. The reaction with sodium hydrogen carbonate solution (about *N*/2) was studied by filtering off the sulphur, washing it with sodium hydrogen carbonate solution (it comes through the filter if water is used), oxidising it with fuming nitric acid, and precipitating and weighing as barium sulphate; the filtrate was concentrated and acidified with nitric acid, and silver bromide was precipitated from it and weighed; the filtrate from this was mixed with bromine water and concentrated, and barium sulphate was precipitated from it and weighed. The quantities obtained corresponded within 3—10 per cent. of those required by the equation $2\text{S}_2\text{Br}_2 + 6\text{NaHCO}_3 = 4\text{NaBr} + \text{Na}_2\text{SO}_3 + 3\text{S} + 6\text{CO}_2 + 3\text{H}_2\text{O}$. C. F. B.

Preparation of Alkali Hyposulphites. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 148125).—Sodium or potassium, or their alloys with lead or mercury, react with sulphur dioxide in presence of ether or well-cooled alcohol, forming alkali hyposulphites, which are very stable in contact with air: $2\text{Na} + 2\text{SO}_2 = \text{Na}_2\text{S}_2\text{O}_4$. Zinc hyposulphite has been obtained in an unstable form by NaBr (Abstr., 1900, ii, 13) by the action of zinc on an alcoholic solution of sulphur dioxide, and Moissan has found (Abstr., 1903, ii, 75) that alkali hydrides also react with sulphur dioxide, forming hyposulphites. C. H. D.

Absorption of Nitrogen and other Gases, especially those containing Nitrogen, by Metallic Manganese. ALEXANDER P. LIDOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 1238. Compare Abstr., 1902, 353).—At a high temperature, manganese absorbs nitrogen even

more readily than magnesium does, but a mixture of the latter metal with lime absorbs nitrogen far more readily than one of manganese and lime; in the former mixture, a reaction takes place resulting in the formation of metallic calcium, whilst with manganese and lime no such change occurs.

Manganese also absorbs other gases containing nitrogen, such as cyanogen. Its use in gas analysis is therefore recommended.

T. H. P.

Relations between the Nature of the Arc, its Temperature, and the Yield of Nitric Oxide by the Burning of Atmospheric Nitrogen. FRANZ VON LEPEL (*Ber.*, 1904, **37**, 712—719. Compare Muthmann and Hofer, *Abstr.*, 1903, ii, 206).—By sucking away the gaseous products through porcelain tubes, it was found that the zone of minimum anode activity is quite close to the anode, and conversely, that in the immediate neighbourhood of the cathode the maximum amount of nitric oxide is formed. The arc should be of medium length to obtain the best results, as the yield of nitric oxide is poor with either a short flame and a high temperature or a long flame and a correspondingly low temperature. The time of action should not be too long. The effect of introducing different types of Wehnelt interruptors is dealt with, and the advantages produced by rotating the anode and moistening the cathode with various salts. W. A. D.

Properties of Mixtures of Nitric and Sulphuric Acids. I. A. V. SAPOSCHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 1098—1112).—In order to obtain some idea of the causes of the increased nitrating action of a mixture of nitric and sulphuric acids over that of nitric acid alone, the author has studied such mixtures under various physico-chemical aspects: (1) *Vapour pressure*.—The measurement of the vapour pressures was made by passing a known volume of air through the mixtures and determining the amounts of nitric acid passing off with the air. The presence of 2.77 per cent. of sulphuric acid in a mixture of the acids lowers the vapour pressure of nitric acid (at 25°) from 46.20 to 41.24 mm.; this rapid fall the author considers to be due to conversion of the volatile nitric oxide into the non-volatile nitrosylsulphuric acid. For mixtures of the acids containing 95 to 80 per cent. of nitric acid, the vapour pressure remains almost constant, whilst from 70 to 30—25 per cent. the pressure falls from about 39 mm. to about 19.4—16 mm., the curve between these points being very nearly a straight line. At between 25 and 20 per cent. of nitric acid, a point of inflexion occurs in the curve, which afterwards proceeds to the zero of pressure for pure sulphuric acid. Preliminary measurements of the vapour pressure of dilute nitric acid show that the presence of water (14—15 per cent.) in the acid causes a considerable diminution in its vapour pressure, which gradually increases when sulphuric acid is added, until when about 50 per cent. of this acid is present in the mixture the vapour pressure is almost doubled, and indeed about equal to the vapour pressure of pure nitric acid mixed with the same proportion of concentrated sulphuric acid. (2) *Composition of the vapours of mixtures of nitric acid with sulphuric*

acid.—Determination of the composition of the vapours carried off from mixtures of nitric acid and sulphuric acid shows that the principal action of the sulphuric acid is that of removing excess of water from the nitric acid ; any chemical action occurring is limited to the conversion of a portion of the nitric acid into the corresponding anhydride, and this only takes place in presence of a very large proportion of sulphuric acid. (3) *Specific gravity*.—This magnitude gradually increases by the addition to nitric acid of sulphuric acid until about 89 per cent. of the latter is present, when a maximum is reached ; after this, it falls to the value for pure sulphuric acid. This maximum value may be contributed to by two causes : firstly, a diminution of the number of molecules of nitric acid present, owing to the dehydration by the sulphuric acid, and secondly, the increase which is known to take place in the sp. gr. of sulphuric acid when small proportions of water are added to it. (4) *Electrical conductivity*.—The variation of the specific conductivity of mixtures of these acids with the proportion of sulphuric acid present is of a very complex character, the curve presenting a minimum, a maximum, and a point of inflexion. The curve for aqueous sulphuric acid is also given, and is likewise of a complex nature. T. H. P.

Action of Carbon Dioxide on Solutions of Sodium Nitrite. CHARLES MARIE and R. MARQUIS (*Compt. rend.*, 1904, 138, 367).—Meunier's conclusion that carbon dioxide does not displace nitrous acid from solutions of its sodium salt (compare this vol., i, 208) is opposed to results previously obtained by the authors (compare Abstr., 1896, i, 403 ; ii, 364), who have therefore repeated some simple experiments which prove incontrovertibly that carbon dioxide displaces nitrous acid from solutions of sodium nitrite. (1) Pure carbon dioxide was passed into a solution of sodium nitrite containing potassium iodide and starch paste ; the development of a blue colour indicated the liberation of iodine by nitrous acid. (2) A solution of potassium iodide and sodium nitrite produced no coloration in chloroform, whilst a similar solution saturated with carbon dioxide caused the chloroform to become violet. (3) A solution of potassium iodide and starch was coloured blue by carbon dioxide which had previously passed through a solution of sodium nitrite. M. A. W.

Action of Carbon Dioxide on Solutions of Sodium Nitrite. LOUIS MEUNIER (*Compt. rend.*, 1904, 138, 502—503. Compare this vol., i, 208).—The author maintains his former conclusion that carbon dioxide does not liberate nitrous acid from aqueous solutions of pure sodium nitrite. The formation of nitrous acid observed in the first two of the experiments quoted by Marie and Marquis as affording evidence to the contrary (preceding abstract) is due to the presence of potassium iodide. With reference to the third experiment, the author suggests that the sodium nitrite used contained small quantities of halogen salts, which behaved similarly to the potassium iodide in the first two experiments. M. A. W.

Molecular Weight of Solid Phosphorus Hydride. RUDOLF SCHENCK and ERNST BUCK (*Ber.*, 1904, 37, 915—917).—The molecular

weight of solid phosphorus hydride, $(P_2H)_n$, has been determined by the cryoscopic method in yellow phosphorus solution. The values obtained agree with the formula $C_{12}H_6$. The molecular depression for yellow phosphorus was determined by the aid of naphthalene and found to be 332; the theoretical value obtained by Hell (*Zeit. physikal. Chem.*, 1893, 12, 196) from Van't Hoff's equation is 384. J. J. S.

Production of Phosphorus Sulphides in the Cold. R. BOULOUCH (*Compt. rend.*, 1904, 138, 363—365).—Whilst phosphorus and sulphur combine at high temperatures to form most of the phosphorus sulphides, no compounds are formed by the direct action of the two elements below 100° (compare Abstr., 1902, ii, 560). On the other hand, Dervin obtained the disulphide, P_3S_6 , and the sulphide, P_8S_{11} , by prolonged (1—2 months) action of light on mixtures of phosphorus sesquisulphide, P_4S_3 , and sulphur in carbon disulphide solution (compare Dervin, Abstr., 1884, 1259), and the author finds that the reaction is much accelerated by the addition of a little iodine to the carbon disulphide solutions, but under these conditions yellow crystals separate from the solution after one or two days which correspond with the formula P_4S_5 . The disulphide, P_3S_6 , is obtained after one or two days by the action of light on solutions of phosphorus and excess of sulphur in carbon disulphide in the presence of iodine; the addition of phosphorus causes this compound to break down into the lower sulphides of phosphorus. On the other hand, the action of sulphur on excess of phosphorus in carbon disulphide containing iodine is less rapid, and the yellow, crystalline product corresponds with the formula P_8S_5 , which may not, however, be a definite compound. M. A. W.

Action of Heat and Light on Mixtures of Phosphorus Sesquisulphide and Sulphur in Carbon Disulphide Solution. E. DERVIN (*Compt. rend.*, 1904, 138, 365—366. Compare preceding abstract).—In view of the results obtained by Boulouch by the action of light on mixtures of phosphorus sesquichloride and sulphur in carbon disulphide solution in the presence of iodine, the author has re-examined the action of light and heat on similar solutions in the absence of iodine, and the result confirms his original conclusions (compare Abstr., 1884, 1259), namely, phosphorus sesquisulphide and sulphur in carbon disulphide solution interact slowly (1 to 2 months) under the influence of sunlight, but rapidly (2 hours) when heated at 210° to form a mixture of Seiler and Ramme's phosphorus disulphide, P_3S_6 , crystallising in yellow, transparent needles, and spherical, crystalline masses which correspond with the formula P_8S_{11} , or more probably $P_4S_3 \cdot 2P_2S_4$. The separation of the two substances is effected by hand sorting, and by heating the crystalline magma to 100° in a sealed tube containing carbon disulphide, when the magma disappears, and crystals of P_3S_6 form in the upper part of the tube, which is kept cool by means of a current of cold water. M. A. W.

Trithio-oxyarsenic Acid. LEROY W. MCCAY and WILLIAM FOSTER, jun. (*Ber.*, 1904, 37, 573—574).—By the action of magnesia

on freshly prepared arsenic pentasulphide, suspended in water, a solution was obtained from which, after removing the magnesium by means of sodium hydroxide, the normal sodium salt of trithio-oxyarsenic acid was isolated. By adding alcohol to the cold solution, the salt slowly separates in feathery crystals, and can be recrystallised from water containing a little sodium hydroxide; in each case, the salt has the composition $\text{Na}_3\text{AsOS}_3 \cdot 11\text{H}_2\text{O}$.

T. M. L.

Defects of Uncarburetted Water-gas as Fuel for Laboratory Use. MASUME CHIKASHIGE and HITOSHI MATSUMOTO (*J. Soc. Chem. Ind.*, 1904, 23, 50—53).—The authors are convinced of the unfitness of this gas for the ordinary purposes of the laboratory. A much larger volume of gas must be supplied to the burner to give a flame of the usual size. Copper air-baths and water-baths are rapidly destroyed by the flame, the bottoms of the baths stripping off as cupric oxide. Nickel crucibles are carbonised, even in one operation, to a brittle black substance. The bottoms of platinum vessels become brittle with a white, crystalline appearance, and after repeatedly heating in the flame may fall to pieces spontaneously. A firmly adherent deposit is formed on the surface of porcelain crucibles, increasing their weight, and rendering accurate quantitative work impossible. Under certain conditions, considerable quantities of carbon monoxide escape unconsumed from the flame. The advantages of the gas are its simplicity of manufacture, the high temperature of the flame, and the smokeless character of the latter, no air-passages being necessary to produce a non-luminous flame.

Experiments were made, following the method of Smithells and Ingle (*Trans.*, 1892, 61, 204), to ascertain the order in which the constituents burn in the air-fed flame. The results obtained show that the hydrogen burns before the carbon monoxide mixed with it. It follows that the inner cone of the flame of water-gas, and air is that of burning hydrogen, and that in the outer cone of this flame and also in that of hydrocarbon flames the carbon monoxide must be the last constituent to burn.

W. P. S.

Change of Rock Crystal into the Amorphous Condition. MORDKO HERSCHKOWITSCH (*Zeit. physikal. Chem.*, 1903, 46, 408—414).—It is well known that rock crystal loses its property of double refraction when fused. Sometimes in the course of the change an opaque, milky looking product is obtained, which has a sp. gr. between that of rock crystal (2.651) and that of amorphous quartz (2.204), and consists of a mixture of the two. Fused quartz may become opaque at higher temperatures, and this is shown to be due to the reverse change—amorphous \rightarrow crystalline; at the ordinary temperature, however, the velocity of this change is practically zero. The elasticity and hardness of amorphous quartz are less than those of rock crystal. The index of refraction of amorphous quartz (n_D , 1.45848) is less than that for either ray in the natural quartz. The most refrangible ultra-violet rays pass less readily through amorphous quartz than through rock crystal.

J. C. P.

Emanation of Gases Occluded or Disengaged by Radium Bromide. JAMES DEWAR and PIERRE CURIE (*Compt. rend.*, 1904, 138, 190—192).—0.4 gram of pure dry radium bromide, left for three months in a glass vessel in communication with a Geissler tube exhausted of air, gave off 3 c.c. (at atmospheric pressure) of a gas which was found to be only hydrogen, and due probably to the decomposition of a small quantity of water accidentally introduced with the salt into the tube; the same specimen of radium bromide was heated to fusion in a quartz flask and the occluded gases withdrawn by means of a mercury pump, the larger part of the emanation and the less volatile gases were retained in three small U-tubes placed in liquid air; the rest of the gas collected over mercury measured 2.6 c.c. at atmospheric pressure, it was radioactive and luminous, and after an exposure of three days with a quartz photographic spectroscope gave a discontinuous spectrum consisting of three lines coincident with the three principal bands of nitrogen, 3800, 3580, and 3370 (compare Huggins, this vol., ii, 4). During the three days, the glass of the tube acquired an intense violet colour, and half the gas was absorbed. The spark spectrum of the gas also showed only the bands characteristic of nitrogen, even after condensing the nitrogen by means of liquid hydrogen.

The quartz tube containing the fused radium bromide deprived of all occluded gases was sealed and examined spectroscopically 20 days later by Deslandres, with the result that the gas in the tube gave the entire spectrum of helium, there being no lines of any other gas even after an exposure of 3 hours (compare Ramsay and Soddy, *Abstr.*, 1903, ii, 622).
M. A. W.

Radioactive Gas in the Soil and Water near New Haven. H. A. BUMSTEAD and L. P. WHEELER (*Amer. J. Sci.*, 1904, [iv], 17, 97—111. Compare this vol., ii, 29).—The radioactive gas found in the ground and in the surface water near New Haven seems to be identical with the radium emanation. If any other radioactive constituent is present, it can be in very small amount only. The density of the radium emanation, as determined by its rate of diffusion, is about four times that of carbon dioxide. The authors were unable to obtain the radioactive gas from mercury, recently described by Strutt (*Phil. Mag.*, July, 1903) and are inclined to attribute his results to an impurity in the mercury used.
A. McK.

Preparation of Alkali Oxides. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 147933. Compare *Abstr.*, 1903, ii, 646).—Metallic sodium or potassium is intimately mixed with the peroxide of the same metal, and the powder thus obtained is ignited by means of a heated wire, and is then heated to bright redness. The reaction occurs rapidly, but not explosively, and the walls of the vessel are therefore little attacked. Air must be excluded, especially in the case of potassium, which readily regenerates the peroxide.
C. H. D.

Determination of the Electrochemical Equivalent of Silver. G. VAN DIJK and J. KUNST (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 441—449).—The authors have re-determined the electro-

chemical equivalent of silver. A tangent galvanometer was used for the measurement of the strength of the current, the horizontal intensity of the terrestrial magnetism having been measured before and after the passage of the current. The cathodes consisted of platinum, two of them being cup-shaped, whilst the third was a cylinder ending in a hemisphere; the anode was a silver rod.

The electrolyte was a 20 per cent. neutral solution of silver nitrate. As a mean of 24 determinations, the value obtained was 0.0111818 ± 0.0000004 (mean error).
A. MCK.

Solidification and Transformations of Mixtures of Silver Nitrate and Potassium Nitrate. A. USSOW (*Zeit. anorg. Chem.*, 1904, 38, 419—428).—The temperatures at which mixtures of varying amounts of silver nitrate and potassium nitrate solidified were determined experimentally and the results depicted graphically. At 134.3° , the double salt, $\text{AgNO}_3 \cdot \text{KNO}_3$, is in equilibrium with potassium nitrate and the solution, and this equilibrium is always attained in all mixtures containing between 46 and 100 per cent. of potassium nitrate.
A. MCK.

Solubility of some Sparingly Soluble Silver Salts. RICHARD ABEGG [with A. J. Cox] (*Zeit. physikal. Chem.*, 1903, 46, 1—12).—Using the ordinary compensation method, the authors have determined the potential differences at electrodes of the type $\text{Ag} | \text{AgX}, N/10\text{MX}$, where AgX is a sparingly soluble silver salt, and MX is a soluble salt of the metal M with the same anion. According to Nernst's theory, it is then possible to calculate the solubility of AgX . With the following soluble electrolytes and the corresponding silver salts as depolarisers, the silver potentials found were (in volts): $\text{KBr} - 0.133$; $\text{KCNS} - 0.127$; $\text{KCl} + 0.015$; $\frac{1}{2}\text{Ba}(\text{OH})_2 + 0.111$; $\frac{1}{2}\text{Na}_2\text{CO}_3 + 0.226$; $\frac{1}{2}\text{K}_2\text{CrO}_4 + 0.227$; $\frac{1}{2}\text{Na}_2\text{B}_4\text{O}_7 + 0.343$. The order of the potential differences gives the order of solubility of the silver salts only where these are of the same dissociating type. The authors have tabulated all the values found by different investigators for the solubility of sparingly soluble silver compounds.
J. C. P.

Action of Carbon on Quicklime at the Temperature of Fusion of Platinum. HENRI MOISSAN (*Compt. rend.*, 1904, 138, 243—245).—A mixture of quicklime and sugar carbon in the proportion required to form calcium carbide, CaC_2 , was heated to the temperature at which platinum fuses by placing it in a graphite boat in a quartz tube in an oxyhydrogen blowpipe furnace (compare Abstr., 1902, ii, 122); at this temperature, no calcium carbide was formed, but the quartz tube softened and small crystals of calcium silicate were detected on the surface of the lime, showing that at the temperature of 1200° silica has an appreciable vapour tension, a characteristic which seriously limits its application to high temperature reactions. Some crystals of calcium carbide heated in a quartz tube in the same furnace showed no signs of liquefaction; the fusion point of calcium carbide is therefore higher than that of platinum. The author has previously shown that platinum melts at the temperature at which

fused calcium carbide solidifies (compare Abstr., 1894, i, 313), and similar results were obtained when a platinum iridium alloy replaced the platinum.
M. A. W.

Hardening of Barium Sulphate. PAUL ROHLAND (*Zeit. anorg. Chem.*, 1904, 38, 311—318. Compare Abstr., 1903, ii, 539).—Barium sulphate does not undergo reactions involving hydration or hardening owing to its sparing solubility in water. The solubility of barium sulphate in water is, however, increased by the addition of aluminium chloride, ferric chloride, magnesium chloride, or ammonium nitrate. The hardening of barium sulphate may be effected by the same method as is used in the case of kaolin. Finely-divided heavy spar is intimately mixed with a 10 per cent. solution of one of the chlorides enumerated, when a plastic mass, containing 12—13 per cent of water and 1.1—1.4 per cent. of the chloride used is obtained. The total loss on heating at 580° was 11.6 per cent.

The theory of the hardening of barium sulphate is discussed.

A. McK.

Glucinum Compounds. I. FRITZ HABER and G. VAN OORDT (*Zeit. anorg. Chem.*, 1904, 38, 377—398).—Glucinum hydroxide, when freshly precipitated, is gelatinous, readily absorbs carbon dioxide, and is easily soluble in potassium carbonate, ammonium carbonate, dilute sodium hydroxide, or dilute acids. It loses these properties when it is heated with water, dilute ammonia, or alkali carbonates, or even when it is allowed to remain at the ordinary temperature. The transformation is particularly rapid when hot alkalis are used; the influence of the concentration of the alkali in promoting the change has been studied. The contradictions found in the literature respecting glucinum hydroxide are to be ascribed to the different conditions employed by the various investigators for its preparation.

A. McK.

Specific Gravity of Zinc Chloride. GREGORY P. BAXTER and ARTHUR BECKET LAMB (*Amer. Chem. J.*, 1904, 31, 229—235).—The sp. gr. of pure dry zinc chloride, prepared by igniting the double ammonium salt, $\text{ZnCl}_2 \cdot 3\text{NH}_4\text{Cl}$, in a current of dry hydrogen chloride, was determined by means of the pyknometer described in the following abstract, pure toluene being employed as the liquid. The average of five determinations gave the sp. gr. 2.907 at 25°/4°.

E. G.

Specific Gravities of Cadmium Chloride and Cadmium Bromide. GREGORY P. BAXTER and MURRAY ARNOLD HINES (*Amer. Chem. J.*, 1904, 31, 220—228).—The determinations described in this paper were carried out with a special form of pycnometer, consisting of a weighing bottle provided with two glass stoppers; one of these stoppers was of the ordinary form and was used during the weighing of the salt, whilst the other was furnished with two capillary tubes by means of which the vessel was filled with liquid. A diagram of this apparatus is given.

The liquid employed was carefully purified toluene of sp. gr. 0·86138 at 25°/4°. In order to check the accuracy of the method, the sp. gr. of silver bromide was first determined and found to be 6·478 at 25°/4°.

The sp. gr. of pure dry cadmium chloride, prepared by igniting the double ammonium salt, $\text{CdCl}_2 \cdot \text{NH}_4\text{Cl}$, in a current of dry hydrogen chloride, was found to be 4·049, and that of cadmium bromide 5·196 at 25°/4°. E. G.

A Cadmium Arsenide. ALBERT GRANGER (*Compt. rend.*, 1904, 138, 574—575).—An arsenide of cadmium of the composition Cd_3As_2 is formed by heating metallic cadmium to bright redness in a current of arsenic vapour diluted with hydrogen. The new arsenide is obtained as a sublimate of shining, red octahedra having the sp. gr. 6·211 at 15°. It is attacked by cold dilute nitric acid, aqua regia, chlorine or bromine. S. S.

Basic Lead Salts. DANIEL STRÖMHOLM (*Zeit. anorg. Chem.*, 1904, 38, 429—455. Compare Abstr., 1903, i, 138).—Most of the basic salts described were prepared as follows. A calculated amount of the alkali salt in about $N/10$ solution was added to lead hydroxide and the solution was titrated with $N/50$ sulphuric acid as soon as the equilibrium had been established. With further addition of the alkali salt, the alkalinity of the solution remained approximately constant, until, finally, a point was reached when the alkalinity diminished. The salt so prepared was washed by decantation and dried, care being taken to avoid any interaction with carbon dioxide. The majority of the salts described are distinctly crystalline.

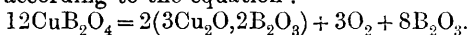
The salt, $6\text{PbO}, \text{PbCl}_2, 2\text{H}_2\text{O}$, crystallises in needles and, when heated, changes in colour from grey to yellow. The salt, $3\text{PbO}, \text{PbCl}_2, \frac{1}{2}\text{H}_2\text{O}$, crystallises in yellow needles. The following salts were prepared: $6\text{PbO}, \text{PbBr}_2, 2\text{H}_2\text{O}$ (white needles); $\text{PbO}, \text{PbBr}_2, \text{H}_2\text{O}$ (needles); $6\text{PbO}, \text{PbI}_2, 2\text{H}_2\text{O}$ (needles); $9\text{PbO}_2, \text{PbI}_2, 2\text{H}_2\text{O}$; $3\text{PbO}, \text{PbI}_2, \text{H}_2\text{O}$; $\text{PbO}, \text{PbI}_2, \text{H}_2\text{O}$; $6\text{PbO}, \text{Pb}(\text{CNS})_2, 2\text{H}_2\text{O}(\text{?})$; $\text{PbO}, \text{Pb}(\text{SCN})_2, \text{H}_2\text{O}$; $3\text{PbO}, \text{Pb}(\text{BrO}_3)_2, 2\text{H}_2\text{O}$; $3\text{PbO}, \text{Pb}(\text{IO}_3)_2, 2\text{H}_2\text{O}$; $3\text{PbO}, \text{PbSO}_4, \text{H}_2\text{O}$; $\text{PbO}, \text{PbSO}_4$; $3\text{PbO}, \text{PbSeO}_4, \text{H}_2\text{O}$; $3\text{PbO}, \text{PbCrO}_4, \text{H}_2\text{O}$; $\text{PbO}, \text{PbCrO}_4$; $15\text{PbO}, 2\text{As}_2\text{O}_5(\text{?})$; $3\text{PbO}, 4\text{PbCO}_3, 2\text{H}_2\text{O}$; $7\text{PbO}, 3\text{PbC}_2\text{O}_4, \text{H}_2\text{O}(\text{?})$; $3\text{PbOPb}[\text{C}_6\text{H}_2(\text{NO}_2)_3\text{O}]_2, 2\frac{1}{2}\text{H}_2\text{O}$. The constitution of these salts is also discussed. A. McK.

Action of Ammonia on Copper Sulphate Solutions. JAMES LOCKE and JACOB FORSSALL (*Amer. Chem. J.*, 1904, 31, 268—298).—Recent investigations have shown that when ammonia is added to a solution of copper sulphate a complex radicle is formed which contains not more than 4 mols. of ammonia to 1 atom of copper. Dawson and McCrae (*Trans.*, 1900, 77, 1252) obtained results in which the ratio of copper to combined ammonia ($\text{Cu} : \text{NH}_3$) varied from 1:3·14 to 1:3·96. This variation was probably due to the fact that the methods employed did not give the correct values for the concentration of the residual ammonia.

In the experiments now described, the lowering of the vapour pressure of a solution of ammonia produced by the addition of copper sulphate was determined by a modification of Gaus' method (Abstr., 1900, ii, 7), in which a known volume of electrolytic gas is passed through the solution and thence into standard hydrochloric acid. The diminution in the conductivity of the acid as it becomes partially neutralised indicates the amount of ammonia taken up by the gas, and from these data its partial pressure in the solution is calculated. The method is fully described, and a diagram of the apparatus is given. The error introduced due to the solubility of ammonia in copper sulphate solution being less than its solubility in water was estimated and the necessary correction applied.

The results show that in dilute solutions only one complex, $\text{Cu}(\text{NH}_3)_4$, is formed and that practically the whole of the copper in the solution passes into this form. With higher concentrations of the ammonia, a small quantity of a complex, $\text{Cu}(\text{NH}_3)_5$, is produced, and in ammonia solutions of approximately normal strength this amounts to about 3 per cent. of the total copper present. E. G.

Evolution of Oxygen from Cupric Metaborate. W. GUERTLER (*Zeit. anorg. Chem.*, 1904, 38, 456—460).—When an aqueous solution of copper nitrate (1 mol.) and boric acid (2 mols.) is evaporated and the product melted at a temperature not exceeding 950° , cupric metaborate is formed. It crystallises in blue needles, has a degree of hardness of the same order as that of corundum, is insoluble in cold dilute mineral acids and in hydrofluoric acid, but is soluble in hot concentrated hydrochloric acid. When melted, it forms a hard glass, which is soluble in cold dilute acids. Cupric metaborate is more easily prepared by fusing copper nitrate with an excess of boric acid, when two layers are formed, the lower one consisting almost entirely of cupric metaborate. Oxygen is rapidly evolved when cupric metaborate is heated at about 1000° ; oxygen begins to come off at about 875° ; the salt melts at about 970° . Analysis showed that the action probably proceeds according to the equation:



A. McK.

Acid Sulphates of the Rare Earths. BOHUSLAV BRAUNER and JAN PICEK (*Zeit. anorg. Chem.*, 1904, 38, 322—341).—An historical survey of the acid sulphates of the rare earths is first given.

In attempting to prepare cerium hydrogen sulphate by Wyruboff's directions, the authors found it impossible to separate the crystals of the acid salt from adhering sulphuric acid at the ordinary pressure without causing decomposition of the salt. The separation could, however, be effected by heating under diminished pressure at a temperature not sufficiently high to cause decomposition of the sulphate.

Cerium hydrogen sulphate, $\text{Ce}(\text{SO}_4\text{H})_3$, was prepared by dissolving normal cerium sulphate in ice-cold water and then adding an excess of sulphuric acid. The acid salt which separates may occasionally be contaminated with the hydrate of the normal salt, which is, however, readily converted into the acid salt by heating. The acid salt was

freed from sulphuric acid in a Sprengel vacuum at 130° ; it forms colourless, glistening needles.

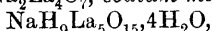
Lanthanum hydrogen sulphate, $\text{La}(\text{SO}_4\text{H})_3$, forms colourless, silky needles. *Praseodymium hydrogen sulphate*, $\text{Pr}(\text{SO}_4\text{H})_3$, forms green, silky needles. *Neodymium hydrogen sulphate*, $\text{Nd}(\text{SO}_4\text{H})_3$, forms rose-coloured, silky needles. *Samarium hydrogen sulphate*, $\text{Sm}(\text{SO}_4\text{H})_3$, forms golden, silky needles. *Yttrium hydrogen sulphate*, $\text{Y}_2(\text{SO}_4\text{H})_3$, forms colourless pyramids. *Thorium hydrogen sulphate*, $\text{ThH}_2(\text{SO}_4)_3$, is formed with difficulty owing to the sparing solubility of normal thorium sulphate in concentrated sulphuric acid. The salt is different from the compound $2\text{Th}(\text{SO}_4)_2 \cdot \text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, which Manuelli and Gasparinetti claim to have prepared (Abstr., 1903, ii, 375).

The decomposition of these acid salts in a Sprengel vacuum has also been studied. Decomposition does not begin in any case below 180° ; above this temperature, sulphuric acid is formed. No pyrosulphate was formed. A. McK.

Chemistry of the Rare Earths. Lanthanum Alums. New Double Sulphates. CHARLES BASKERVILLE and EUGENE G. MOSS (*J. Amer. Chem. Soc.*, 1904, 26, 67—71).—A number of experiments have been carried out with the object of preparing lanthanum alums. Owing, however, to the formation of a comparatively insoluble hydrate of lanthanum sulphate, $\text{La}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, and to the separation of sparingly soluble double sulphates, the alums could not be obtained. The following double salts were prepared and analysed:

$\text{La}_2(\text{SO}_4)_3 \cdot \text{Rb}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$; $\text{La}_2(\text{SO}_4)_3 \cdot \text{Cs}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$; $\text{La}_2(\text{SO}_4)_3 \cdot \text{Rb}_2\text{SO}_4 \cdot 3\text{La}_2(\text{SO}_4)_3 \cdot 2\text{Rb}_2\text{SO}_4$; and $3\text{La}_2(\text{SO}_4)_3 \cdot 2\text{Cs}_2\text{SO}_4$. E. G.

Chemistry of the Rare Earths. Lanthanates. CHARLES BASKERVILLE and GEORGE F. CATLETT (*J. Amer. Chem. Soc.*, 1904, 26, 75—80).—Lanthanates and metalanthanates may be obtained by fusing lanthanum oxide with an alkali carbonate or by heating the oxide with a concentrated solution of an alkali hydroxide at 100° . *Sodium tetralanthanate*, $\text{Na}_2\text{La}_4\text{O}_7$, *sodium metalanthanate*,



lithium metalanthanate, $\text{LiH}_9\text{La}_5\text{O}_{15} \cdot 2\text{H}_2\text{O}$, *barium metalanthanate*, $\text{Ba}(\text{H}_9\text{La}_5\text{O}_{15})_2$, and *potassium metalanthanate* were prepared and analysed. These compounds are of no value for the separation and purification of lanthanum. E. G.

Chemistry of the Rare Earths. Neodymium; Preparation of Pure Material, and Efforts to Decompose it into its Constituents. CHARLES BASKERVILLE and RESTON STEVENSON (*J. Amer. Chem. Soc.*, 1904, 26, 54—64).—Neodymium may be freed from lanthanum by saturating a solution of neodymium chloride with hydrogen chloride until no more crystals separate. The crystals are redissolved and reprecipitated in the same way; after seven such precipitations, the final product is absolutely free from lanthanum.

The pure neodymium compound thus obtained was used in unsuccessful attempts to prove its complexity. The methods employed

were as follows. Fractional precipitation with hydrogen chloride; partial decomposition by fusing the double alkali nitrates; precipitation with ammonium oxalate; solution of the hydroxide in ammonium carbonate and precipitation with acetic acid; fractional precipitation with aniline, benzylamine, piperidine, or phenylhydrazine. E. G.

Chemistry of the Rare Earths. Praseodymium and its Citrate. CHARLES BASKERVILLE and J. W. TURRENTINE (*J. Amer. Chem. Soc.*, 1904, 26, 46—53).—The following method is recommended for the rapid preparation of pure praseodymium compounds. Praseodymium ammonium nitrate containing about 10 per cent. of lanthanum is converted into the hydroxide, which is washed free from ammonium salts and afterwards added to a concentrated aqueous solution of citric acid until the solution is saturated. On heating this solution, a pale green, amorphous precipitate is produced, which is collected, washed with hot water, and afterwards dried. *Praseodymium citrate* is thus obtained as a loose, amorphous powder of a pale green colour.

Attempts were also made to prepare pure praseodymium compounds by means of potassium iodate, hydrofluoric acid, hydrochloric acid, formaldehyde, potassium pyrosulphate, alkali hydroxides, sodium peroxide, or by the formation of alums, but in all cases the results were unsatisfactory. E. G.

Chemistry of the Rare Earths. Attempts to prepare Praseodymium and Neodymium Alums. New Double Sulphates. CHARLES BASKERVILLE and HAZEL HOLLAND (*J. Amer. Chem. Soc.*, 1904, 26, 71—75).—Attempts to prepare praseodymium and neodymium alums by mixing solutions of their sulphates with varying proportions of alkali sulphates were unsuccessful. The following double salts were obtained: $\text{Pr}_2(\text{SO}_4)_3 \cdot \text{Cs}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$; $\text{Pr}_2(\text{SO}_4)_3 \cdot \text{Cs}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$; and $\text{Nd}_2(\text{SO}_4)_3 \cdot \text{Cs}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$. E. G.

Aluminium Powder and the Oxidation of Aluminium. ÉMILE KOHN-ABREST (*Bull. Soc. chim.*, 1904, [iii], 31, 232—239).—The percentage composition of a commercial specimen of aluminium powder, previously freed from fat by extraction with ether, was found to be: aluminium and iron, 91.2; alumina, 5.8; silica, 1.3; graphitoidal silicon and other insoluble matter, 0.4; carbon, 0.23; moisture and loss, 1.07.

The aluminium was estimated either by (1) collecting and weighing the water produced by passing the hydrogen evolved by the solution of a known weight of the aluminium powder in dilute hydrochloric acid over heated cupric oxide, or (2) by a modification of Wahl's method of estimating metallic zinc in zinc dust (Abstr., 1898, ii, 190).

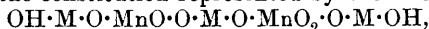
It was found possible to estimate directly the alumina and silica in the powder by heating the latter in air at a temperature above 175° for 12 hours, the alumina being thereby rendered insoluble in hydrochloric acid. The alumina produced by this treatment was corrected for by observing the increase in weight which resulted from the heat-

ing and assuming that this was due to the conversion of aluminium into alumina.

When aluminium powder is added to freshly precipitated aluminium hydroxide, suspended in water containing ammonia, it appears to be absorbed by the hydroxide with the formation of a suboxide. This change also occurs partially and slowly in presence of ammonium chloride. It is suggested that the suboxide is analogous in constitution to the lower chloride and sulphate of aluminium described by Berzelius and others.

T. A. H.

Mangani-manganates of the Alkaline Earths. VICTOR AUGER and M. BILLY (*Compt. rend.*, 1904, 138, 500—502).—The substances hitherto described as manganates of the alkaline earths are not pure compounds. Dulaurier's calcium manganate, for example (*Chem. News*, 1869, 20, 240), is only a mixture of calcium carbonate, manganese dioxide, and calcium manganate. Pure compounds of the type $M_3Mn_2O_8 \cdot H_2O$ can be obtained by fusing at a suitable temperature (180° to 250°) mixtures of the hydroxide of the alkaline earth, sodium and potassium nitrates, and potassium permanganate; the salts probably have the constitution represented by the formula



and are therefore to be regarded as *mangani-manganates*.

Barium mangani-manganate, $Ba_3Mn_2O_8 \cdot H_2O$, identical with Cassel's green or Rosenstiehl's "basic barium manganate" (*J. Pharm. Chim.*, 1864, [iii], 46, 344), is most conveniently prepared by the general method given above; it is a green powder, insoluble in water, and can be heated to redness without losing its water of hydration.

M. A. W.

Sodium Ferric Sulphates. ANTON SKRABAL (*Zeit. anorg. Chem.*, 1904, 38, 319—321).—When a solution of ferric sulphate, containing a little sulphuric acid, is gradually heated on a boiling water-bath with an excess of Glauber's salt, *basic sodium ferric sulphate* of the composition $2Na_2O, Fe_2O_3, 4SO_3, 7H_2O$ separates; it forms yellow, silky crystals and is soluble in water with difficulty; it is decomposed by water. *Sodium ferric sulphate*, $3Na_2O, Fe_2O_3, 6SO_3, 6H_2O$, prepared by first heating Glauber's salt until it melts in its water of crystallisation and then adding ferric sulphate and concentrated sulphuric acid, is colourless and is slowly dissolved by water with decomposition.

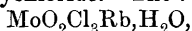
A. McK.

Allotropic Transformations of Nickel Steels. OCTAVE BOUDOUARD (*Compt. rend.*, 1904, 138, 370—371).—By means of a thermoelectric method previously described (compare this vol., ii, 127), the author has determined the temperatures at which certain nickel steels undergo molecular transformation. The steels employed were those already examined by Guillet with regard to their micrographical and mechanical properties (compare Guillet, *Abstr.*, 1903, ii, 267, 650). The temperatures of molecular transformation were indicated by irregularities on the curve obtained by plotting as abscissæ the temperature of the bar of steel under investigation against the difference of potential of thermoelectrical origin between the two

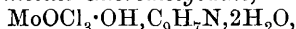
extremities of the bar as ordinates. The results obtained with two series of steels containing 0.2 and 0.8 per cent. of carbon respectively, with a proportion of nickel varying from 2 to 30 per cent. in each series, are given; only those steels with a low nickel content give curves which exhibit irregularities. M. A. W.

Solvent Power and Electrical Conductivity of Liquid Nickel Carbonyl. ALWIN MITTASCH (*Zeit. physikal. Chem.*, 1903, 46, 37—42).—Numbers of inorganic and partly organic electrolytes have been found to be practically insoluble in nickel carbonyl, and the conductivity of the latter (1×10^{-9}) is accordingly affected only to a very slight extent by shaking with these electrolytes. Some organic non electrolytes, such as camphor and alcohol, are more readily soluble. It is noteworthy that Apt finds the dielectric constant of liquid nickel carbonyl to be as low as 2.2. J. C. P.

Chlorinated Molybdates and the Acids from which they are derived. RUDOLF F. WEINLAND and W. KNÖLL (*Ber.*, 1904, 37, 569—573).—*Cæsium chloromolybdate*, $\text{MoO}_2\text{Cl}_3\text{Cs}, \text{H}_2\text{O}$, prepared by the action of cæsium chloride on a solution of molybdic acid in hydrochloric acid, forms small, prismatic, pale greenish-yellow crystals, and on heating liberates water, hydrogen chloride, and finally some colourless molybdenum oxychloride. The *rubidium salt*,

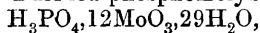


forms small, flat, well-formed prisms. A *potassium salt* also appears to exist. *Pyridine chloromolybdate*, $\text{MoOCl}_3 \cdot \text{OH}, \text{C}_5\text{H}_5\text{N}, 2\text{H}_2\text{O}$, forms colourless flakes. *Quinoline chloromolybdate*,



forms colourless flakes, but separates from concentrated hydrochloric acid in needles. *Chloromolybdic acid*, $\text{MoOCl}_2 \cdot \text{OH}, 7(?)\text{H}_2\text{O}$, prepared by cooling a solution of molybdic acid saturated with hydrogen chloride, was also found to separate in attempting to prepare the calcium, magnesium, and ammonium salts; it forms flat prisms, decomposes in the air in the course of a few minutes, and slowly effloresces over sulphuric acid. T. M. L.

Yellow Phosphomolybdic Acid. ARTURO MIOLATI (*Gazzetta*, 1903, 33, ii, 335—348).—The author has repeated many of the measurements made by Levi and Spelta (*Abstr.*, 1903, ii, 731), but with different results. Purified phosphomolybdic acid,



on titration with sodium hydroxide, using phenolphthalein or litmus as indicator, is found to contain 26, not 27 displaceable hydrogen atoms; this fact is explained by assuming that 24 of the mols. of alkali required for neutralisation are utilised by the 12MoO_3 , and that phosphoric acid behaves in a normal manner as a dibasic acid. Levi and Spelta's assumption would require phosphoric acid to be a tribasic acid in presence of the indicators named. The variation in the electrical conductivity of phosphomolybdic acid in aqueous solution with increasing dilution does not correspond with that of a tribasic acid, even assuming that the complex compound is hydrolysed

into phosphoric and molybdic acids; it appears rather that the phosphomolybdic acid splits off molybdic acid in solution, retaining phosphoric acid in the form of another complex with fewer MoO_3 groups.

From a study of the electrical conductivity of the acid during neutralisation, it appears that the acid is hexabasic; the conductivity continually diminishes until 6 mols. of sodium hydroxide have been added, subsequent to which there is a continuous and steady increase until 26 mols. are present, when each additional mol. of alkali causes an abnormally large increase. It is probable that by any excess of alkali over the six mols. required for neutralisation the hexabasic acid is resolved progressively into phosphoric and molybdic acids. The change of conductivity of a solution having the composition $\text{H}_3\text{PO}_4, 12\text{MoO}_3, 6\text{NaOH}$, with increasing dilution agrees well with that of a normal salt of a hexabasic acid normally dissociated.

W. A. D.

Solubility and Decomposition of Double Salts in Water. III. EBERHARD RIMBACH [with H. BÜRGER and A. GREWE] (*Ber.*, 1904, 37, 461—487. Compare Abstr., 1898, ii, 158; 1902, ii, 306).—The decomposition of various uranyl double salts by water at different temperatures has been determined quantitatively. The uranyl double salts examined are analogous to the cadmium double chlorides previously described (*loc. cit.*).

Solubility determinations were conducted with the pure double salts, and the composition of the solutions, obtained at varying temperatures, was determined analytically.

Uranyl potassium chloride, $\text{UO}_2\text{Cl}_2, 2\text{KCl}, 2\text{H}_2\text{O}$, undergoes decomposition at temperatures below 60° in such a manner that the saturated solution contains an excess of uranyl chloride, whilst the solid in contact with the solution consists of uranyl potassium chloride and potassium chloride. Above 60° , the composition of the saturated solution is identical with that of the solid, and from the saturated solution the double salt may be obtained pure when the proper temperature conditions are observed. When a concentrated aqueous solution, containing uranyl and potassium chlorides in the molecular proportions 1 : 2 respectively, and containing also at least 15 per cent. of hydrochloric acid, is allowed to crystallise, the decomposition of the double salt, which, as noted above, occurs at temperatures below 60° , does not take place.

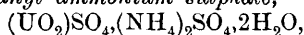
Uranyl ammonium chloride suffers decomposition in an analogous manner to uranyl potassium chloride.

Uranyl rubidium chloride, $\text{UO}_2\text{Cl}_2, 2\text{RbCl}, 2\text{H}_2\text{O}$, is isomorphous with the potassium and ammonium salts, but differs from them in its behaviour towards water, since it remains undecomposed, both at high and low temperatures. Uranyl caesium chloride, $\text{UO}_2\text{Cl}_2, 2\text{CsCl}$, behaves similarly.

Uranyl tetramethylammonium chloride, $\text{UO}_2\text{Cl}_2, 2\text{NMe}_4\text{Cl}$, and *uranyl-tetraethylammonium chloride*, $\text{UO}_2\text{Cl}_2, 2\text{NEt}_4\text{Cl}$, are not decomposed by water. *Uranyl potassium nitrate*, $\text{UO}_2(\text{NO}_3)_2, \text{KNO}_3$, prepared from potassium diuranate and a large excess of nitric acid, is very hygro-

scopic. At temperatures below 60° , the solid phases, uranyl potassium nitrate and potassium nitrate, are formed, whilst the supernatant saturated solution is enriched by uranyl nitrate. At about 60° , the end of the transition interval is reached. The behaviour of *uranyl ammonium nitrate*, $\text{UO}_2(\text{NO}_3)_2 \cdot \text{NH}_4\text{NO}_3$, is similar. *Uranyl rubidium nitrate*, $\text{UO}_2(\text{NO}_3)_2 \cdot \text{RbNO}_3$, prepared from uranyl nitrate (1 mol.) and rubidium nitrate (1 mol.) dissolved in excess of nitric acid, is soluble without decomposition at 80° . *Uranyl caesium nitrate*, $\text{UO}_2(\text{NO}_3)_2 \cdot \text{CsNO}_3$, like the analogous salts, is decomposed at low temperatures.

Uranyl potassium sulphate, $(\text{UO}_2)\text{SO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, prepared by dissolving potassium diuranate in sulphuric acid or by allowing an aqueous solution containing molecular properties of the two components to crystallise under diminished pressure, is stable towards water, as are also *uranyl ammonium sulphate*,

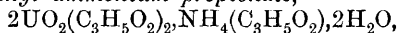


and *uranyl rubidium sulphate*, $(\text{UO}_2)\text{SO}_4 \cdot \text{Rb}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$. *Uranyl dipotassium sulphate*, $(\text{UO}_2)\text{SO}_4 \cdot 2\text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, prepared by dissolving uranyl sulphate in an excess of potassium sulphate solution and then crystallising from the hot solution, is decomposed by water at lower temperatures, the solid phases consisting of the di- and mono-salts, whilst the solution is enriched in potassium sulphate. At 80° , the transition interval is not quite attained.

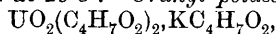
Uranyl hydroxylamine sulphate, $2(\text{UO}_2)\text{SO}_4 \cdot (\text{NH}_2 \cdot \text{OH})_2 \cdot \text{H}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$, prepared from a solution of uranyl sulphate and hydroxylamine sulphate in molecular proportions, separates in yellowish-green aggregates. It appears to be stable towards water at the ordinary temperature.

Uranyl sodium chromate, $2(\text{UO}_2)\text{CrO}_4 \cdot \text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$, is undecomposed by water at 20° . Uranyl potassium arsenate, $(\text{UO}_2)\text{KAsO}_4 \cdot 3\frac{1}{2}\text{H}_2\text{O}$, is a yellow powder, which is stable towards water.

Uranyl potassium propionate, $\text{UO}_2(\text{C}_3\text{H}_5\text{O}_2)_2 \cdot \text{KC}_3\text{H}_5\text{O}_2$, is decomposed by water at 29.4° , potassium propionate going into solution and the solid phases consisting of uranyl propionate and uranyl potassium propionate. *Uranyl ammonium propionate*,



is stable towards water at 29.8° . *Uranyl potassium butyrate*,



and *uranyl potassium valerate*, $\text{UO}_2(\text{C}_5\text{H}_9\text{O}_2)_2 \cdot \text{KC}_5\text{H}_9\text{O}_2 \cdot 2\text{H}_2\text{O}$, suffer decomposition at the ordinary temperature.

The compounds examined, more particularly the double nitrates, were fluorescent. The potassium and rubidium double sulphates and the potassium, ammonium, and rubidium double nitrates exhibited radioactivity.

Crystallographic measurements of several of the compounds described are quoted.

A. McK.

Preparation and Properties of Some New Fluorine Compounds. OTTO RUFF, WILHELM PLATO, and, in part, HUGO GRAF (*Ber.*, 1904, 37, 673—683. Compare *Abstr.*, 1903, ii, 550).—The fluorides described have been prepared by the action of anhydrous hydrogen fluoride on the corresponding chlorides; owing to the relatively high

volatility of the hydrogen chloride formed and the presence of an excess of hydrogen fluoride, the reversible change expressed by the equation $x(\text{HF})_2 + \text{MCl}_n \rightleftharpoons \text{MF}_n + 2x\text{HCl}$ takes place in one direction only. The hydrogen fluoride was prepared and the experiments carried out in special platinum apparatus, for the details of which the original should be consulted.

Titanium tetrafluoride (*loc. cit.*) boils at 284° (corr.), has a sp. gr. 2.798 at $20.5^\circ/4^\circ$, and a vapour density of 129.

Antimony pentafluoride, SbF_5 , is a colourless, viscid liquid, which solidifies when cooled; it is very hygroscopic, forming a hydrate, $\text{SbF}_5 \cdot 2\text{H}_2\text{O}$, boils at 155° , and has a sp. gr. 2.993 at $22.7^\circ/4^\circ$.

Antimony pentafluoride diantimony trifluoride, Sb_3F_{11} , prepared by distilling a mixture of the penta- and tri-fluorides, is a hygroscopic, colourless, transparent, crystalline substance, which boils at 390° , and has a sp. gr. 4.188 at $21^\circ/4^\circ$. When the trifluoride is present in excess, antimony pentafluoride-penta-antimony trifluoride, boiling at about 384° (corr.), is formed.

Tin tetrafluoride is a hygroscopic, crystalline substance; it boils at 705° , subliming below this temperature, and has a sp. gr. 4.78 at $19^\circ/4^\circ$.

It is worthy of note that the molecular volume of these fluorine compounds is very much less than that of the corresponding chlorides.

E. F. A.

Constitution and Properties of Vanadium Steels. LÉON GUILLET (*Compt. rend.*, 1904, 138, 367—369).—According to their micrographical properties, vanadium steels may be divided into three groups: (1) those containing 0.200 per cent. of carbon and less than 0.7 per cent. of vanadium, which present the same structure as the carbon steels; (2) those containing 0.200 or 0.800 per cent. of carbon and 0.7 to 3 per cent. of vanadium, which exhibit perlite or carbide structure; (3) those containing more than 3 per cent. of vanadium, in which all the carbon is combined as vanadium carbide or a double carbide of vanadium and iron. The steels belonging to the first two groups have a breaking weight and elastic limit higher than those of ordinary steels with the same percentage of carbon, but they are harder and more fragile, whilst the steels of the third group have a very low breaking weight and elastic limit and are very fragile.

M. A. W.

Electrolytic Preparation of Salts of Tervalent Vanadium. A. BÜLTEMANN (*Zeit. Elektrochem.*, 1904, 10, 141—143).—A convenient method of carrying out the electrolytic reduction of vanadium salts described by Piccini (*Abstr.*, 1896, ii, 304) and Piccini and Brizzi (*Abstr.*, 1899, ii, 297) is given. A clean lead or platinum cathode and porous diaphragm are used; the current efficiency is practically quantitative with cathodic current densities up to 0.05 ampère per sq. cm. Ammonium vanadium alum, $\text{V}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$, crystallises in blue crystals from a solution containing sulphuric acid, but red crystals are obtained from neutral solutions. The rubidium and caesium alums behave in the same way.

T. E.

Action of the Halogen Acids on Vanadic Acid. FRANK A. GOOCH and R. W. CURTIS (*Amer. J. Sci.*, 1904, [iv], 17, 41—48).—The reducing action of hydrochloric, hydrobromic, and hydriodic acids respectively on vanadic acid has been studied. The extent of reduction is shown to depend on the concentrations of the respective acids. Hydrochloric acid, even in the cold, reduces vanadic acid to the stage corresponding with the tetroxide, and the reduction does not proceed further. The reduction may proceed further when hydrobromic acid is used, whilst with hydriodic acid it may be carried at will to either of the stages, that of the trioxide or that of the tetroxide. A. McK.

Stibine and Yellow Antimony. ALFRED STOCK and OSKAR GUTTMANN (*Ber.*, 1904, 37, 885—900. Compare Abstr., 1901, ii, 556; 1902, ii, 507).—In the preparation of antimony hydride it is essential to add the antimony-magnesium alloy to the dilute hydrochloric acid and not *vice versâ*. An apparatus is described by means of which the finely-divided alloy may be automatically dropped into the acid. The density of the gas is 4.360 at 15° and 754 mm. (air = 1) and is some 2.95 per cent. higher than the normal value, probably owing to the molecular attractions of the heavy molecules. The liquid hydride has a sp. gr. 2.26 at -25° and 2.34 at -50°. At the ordinary temperature, 1 vol. of water dissolves 0.2 vols of gas; 1 vol. of alcohol dissolves 15 vols. of gas; at 0°, 1 vol. of carbon disulphide dissolves 250 vols. of gas. The solutions in alcohol, ether, and benzene are less stable than those in water. The gas may be readily exploded by electric sparks or by heating strongly. When dry, the gas is relatively stable, but when once decomposition starts, the antimony which is deposited rapidly accelerates the action. Light and radium radiations appear to have no effect. The presence of moisture in any form enormously accelerates the decomposition. The liquefied hydride is unstable even at the ordinary temperature. Oxygen and air readily react with the gas at the ordinary temperature, yielding antimony, water, and usually a little free hydrogen. Nitric oxide is reduced to nitrous oxide, nitrogen, and ammonia. Ammonia or hydrogen chloride accelerates the decomposition of the gas into its components. The passage of electric sparks through a mixture of carbon dioxide and antimony hydride leads to the formation of antimony, water, and carbon monoxide. The halogens readily decompose the gas, also sulphur, the antimony haloids, oxidising or alkaline solutions, and all solid alkalis. It is best dried by means of calcium chloride or phosphoric oxide. No compound corresponding with AsH_3 , BBr_3 (Abstr., 1901, ii, 382) has been obtained.

Gaseous antimony hydride is as strong a poison as arsenic hydride, and produces similar effects; white mice die after a few seconds exposure to an atmosphere containing 1 per cent. of the hydride.

A yellow modification of antimony may be obtained by leading a current of air or oxygen into the liquid hydride at -90°. It is extremely unstable, and at -50° is rapidly transformed into the ordinary metallic modification; it is also soluble in carbon disulphide at a little above -90°.

J. J. S.

Mixtures of Antimony Trisulphide and Antimony. HENRI PÉLABON (*Compt. rend.*, 1904, 138, 277—279).—Fused mixtures of

antimony and antimony trisulphide form one or two liquid phases according to the ratio (R) of the antimony sulphide to the total mass of the mixture. When R is less than 0.015, the liquid is homogeneous, and consists of solutions of the trisulphide in antimony, the solidification temperatures of which decrease, as R increases, from 632° , the freezing point of antimony, to 615° , that of a saturated solution of antimony trisulphide in antimony. For values of R between 0.015 and 0.25, the liquid product of fusion consists of two phases, of which the less dense is a solution of antimony in the trisulphide, and the more dense a solution of the trisulphide in antimony; the solidification temperatures, 515° and 615° , of these two liquids remain sensibly the same for all values of R between the limits stated above. Finally, when R is greater than 0.25, the fused mixture is a homogeneous solution of antimony in the trisulphide, and the solidification temperature increases with R from 515° to 555° , the freezing point of the trisulphide. These results are in accordance with those obtained by the author in studying the action of hydrogen on antimony sulphide and of hydrogen sulphide on antimony (compare Abstr., 1900, ii, 352).

The two liquid phases exhibited by solutions containing the trisulphide in the proportions required by $R = 0.015$ to 0.25 are quite distinct, the less dense wets the glass and solidifies to a mass resembling stibnite, only less brittle, whilst the denser liquid does not wet the glass and solidifies to a metallic mass harder than pure antimony.

M. A. W.

Mineralogical Chemistry.

Artificial Production of Krugite. A. GEIGER (*Chem. Centr.*, 1904, i, 604; from *Sitzungsber. K. Akad. Wiss. Berlin*, 1903, 1123—1124).—Attempts to produce krugite $[\text{Ca}_4\text{MgK}_2(\text{SO}_4)_6, 2\text{H}_2\text{O}]$ by the interaction of polyhalite $[\text{Ca}_2\text{MgK}_2(\text{SO}_4)_4, 2\text{H}_2\text{O}]$ and gypsum were without success. Crystals, which are probably orthorhombic, were obtained by the prolonged heating of a solution of magnesium chloride and potassium sulphate with gypsum. L. J. S.

Astrolite, a new Mineral. REINH. REINISCH. (*Centr. Min.*, 1904, 108—115).—The name astrolite (Astrolith) is given to small, greenish-yellow spheres (2—6 mm. diam.) with radially fibrous structure, which occur embedded, either singly or aggregated together, in fragments of black, carbonaceous rock in diabase-tuff at Neumark in Saxon Vogtland. The material has H. $3\frac{1}{2}$, sp. gr. 2.78, and is not attacked by acids. The radially arranged fibres have a good cleavage in one direction, and are pleochroic; their optical characters suggest orthorhombic symmetry. Owing to enclosures of calcite, carbonaceous material, and wedges of the rocky matrix, pure material could not be

obtained for analysis; from the following results, the metasilicate formula, $(\text{Al,Fe})_2\text{Fe}(\text{Na,K})_2(\text{SiO}_3)_5, \text{H}_2\text{O}$, is deduced. No water is lost below 200°

| SiO_2 . | Al_2O_3 | Fe_2O_3 . | FeO . | K_2O . | Na_2O . | H_2O . | CaCO_3 . | Total. |
|------------------|-------------------------|---------------------------|----------------|------------------------|-------------------------|------------------------|-------------------|--------|
| 50.44 | 7.88 | 12.62 | 11.62 | 5.03 | 6.40 | 2.74 | 3.88 | 100.61 |

A detailed description is given of the diabase-tuff and of the various rock fragments embedded in it. The astrolite occurs most frequently in a black, calcareous quartz-schist, but also in anthracitic limestone and in a calcareous shale. L. J. S.

Formation of Tridymite in a Roofing Slate struck by Lightning. ARTHUR SCHWANTKE (*Centr. Min.*, 1904, 87—88).—Microscopic crystals of tridymite were detected in the glassy material which had been produced by the partial fusion of the roofing slate of a building struck by lightning. L. J. S.

Composition of Crystalline Schists from the Alps. PIERRE TERMIER and ANDRÉ LECLÈRE (*Compt. rend.*, 1904, 138, 646—647).—Analyses are given of schists of various kinds from the Belledonne chain. Alkalis are present to the extent of 4—12 per cent., averaging 6 per cent. in the seven analyses; sodium is present as albite, and potassium as muscovite. These rocks having been formed by the regional metamorphism of sedimentary rocks (which contain only small amounts of alkalis), it follows that alkalis must have been introduced during the process of metamorphism. L. J. S.

Salinity of Waters from the Oolites. WALTER W. FISHER (*Analyst*, 1904, 29, 29—40).—The results of the analyses are given of a considerable number of waters from the several geological formations grouped together as "oolites," namely: Kimmeridge clay, Corallian Oolite, Oxford clay and Kelloway Rock, and Cornbrash, Forest Marble and Great Oolite. The waters from the Great Oolite resemble spring waters from the chalk. The dissolved mineral matters are mainly calcium carbonate, with small amounts of magnesium and alkali sulphates and chlorides. The quantity of mineral matters in waters from below the Oxford clay varies considerably, according to the length of flow of the water through the porous beds under the clay. Some of these waters contain peaty matter in solution. As a rule, only small amounts of nitrates are found. The Corallian Oolites yield rather hard waters, containing but small quantities of organic impurities. The nitrates are very variable, depending on the state of the surroundings of the wells. Waters from the Kimmeridge clay are mostly extremely hard.

The results lead to the general conclusion that the uncovered beds of limestone yield calcareous waters of a hard character, whilst the deep beds, especially those covered by clay, give saline or alkaline supplies. The author suggests that the alkali carbonates owe their

origin to the decay of organic matter deposited in or with the rock material, and that the ammonia and organic matters present in saline waters are also due to this organic matter.

W. P. S.

Physiological Chemistry.

Absorption of Oxygen on Alterations of its Partial Pressure in the Alveolar Air. ARNOLD DURIG (*Chem. Centr.*, 1904, i, 390—391; from *Arch. Anat. Physiol., physiol. Abth.*, 1903, 209—369).—The estimations show how widely the limits of proportion of oxygen in the inspired air may vary without materially affecting the amount of oxygen taken up by the organism, and the amount of carbon dioxide excreted.
W. D. H.

Changes in Blood after Exercise. PHILIP B. HAWK (*Amer. J. Physiol.*, 1903, 10, 384—400).—Muscular exercise causes an increase in both red and white corpuscles. This is primarily due to the passage into the circulation of numbers of cells previously lying inactive in various parts of the body.
W. D. H.

Glycerol in the Blood. MAURICE NICLOUX (*Compt. rend. Soc. Biol.*, 1904, 55, 1696—1697, 1698—1700. Compare Abstr., 1903, ii, 337, 438, 560, and this vol., ii, 56; also Mouneyrat, this vol., ii, 56).—Polemical; the author maintains the correctness of his former views against the criticisms of Mouneyrat.
W. D. H.

Blood Coagulation. IV. The Coagulating Power of the Serum. JULES BORDET and OCTAVE GENGOU (*Ann. Inst. Pasteur.*, 1904, 18, 98—115).—Serum brings about the change of fibrinogen into fibrin in the absence of calcium salts; it excites the formation of ferment, this property depending on calcium salts. A number of other well-known facts are also confirmed.
W. D. H.

Tryptic Digestion. HANS RICHARD WEISS (*Zeit. physiol. Chem.*, 1904, 40, 480—491).—The alkali haloids inhibit trypsin activity but little. The most marked effect is obtained with sodium chloride, less with potassium chloride, and less still with the corresponding iodine and bromine compounds. Sodium oxalate and sulphate act more strongly than the chloride. Sodium phosphate favours tryptic action, and borax has no effect.
W. D. H.

Human Pancreatic Juice. KARL GLAESSNER (*Zeit. physiol. Chem.*, 1904, 40, 465—479).—A case in which an operation was performed on the pancreas rendered possible the collection of pancreatic juice. From 500—800 c.c. were secreted daily. It does not contain trypsin but

its zymogen, which is rendered active by the intestinal juice. The steopsin and amylopsin were rendered more active by admixture with both intestinal juice and bile. Amylopsin acts on starch so as to form maltose; the conversion of this into dextrose is performed by the intestinal juice. Disaccharides are not acted on by pancreatic juice. During periods of fasting, the amount of juice, of contained ferments, and of alkalinity are at the minimum. They increase on taking a meal, reach their maximum four hours later, and then sink by the eighth hour after the meal to the fasting level.

W. D. H.

Metabolic Experiments with the End-products of Peptic and Tryptic Digestion. ERNST J. LESSER (*Zeit. Biol.*, 1904, 45, 497—510).—Dogs were fed on the product obtained by a 27 days' peptic digestion of Witte's peptone; this was given mixed with fat. In order to produce putting on of nitrogen or a maintenance of nitrogenous equilibrium, a much larger intake of nitrogen in this form is necessary than is ordinarily the case. The results of similarly feeding with the products of the pancreatic digestion of fibrin are still worse, and the probability is that these substances are not utilisable. The investigation shows little or no evidence of regeneration of proteid from its simplest hydrolytic products.

W. D. H.

Emission of Blondlot's Rays [*n*-Rays] in the Course of the Action of Soluble Ferments. LAMBERT (*Compt. rend.*, 1904, 138, 196—197. Compare Blondlot, *Compt. rend.*, 1903, 136, 735, 1120, 1227, 1421; 137, 166, 684, 729, 831, and Charpentier, *Compt. rend.*, 1903, 137, 1049, 1277).—The digestive action of ferments on proteid matter is accompanied by an emission of *n*-rays, which can be detected by means of a screen of phosphorescent calcium sulphide, either directly or by photography. In one experiment, a portion of fibrin was placed in a tube containing pancreatic juice rendered active by kinase and kept at a temperature of 38°; the *n*-rays were emitted during the process of digestion, but ceased after the fibrin had disappeared. Similar results were obtained when the pancreatic juice was replaced by a dilute solution of pepsin in hydrochloric acid, whilst blank experiments with (1) hydrochloric acid, (2) hydrochloric acid and pepsin, (3) fibrin suspended in a 0.8 per cent. salt solution, gave negative results.

This particular case of emission of *n*-rays during fermentation falls into line with those observed by Blondlot (compare *Compt. rend.*, 1903, 137, 962), the swelling of the fibrin by means of the acid setting up the necessary condition of constraint.

M. A. W.

Calcium and Iron in Nutriment. GUSTAV VON BUNGE (*Zeit. Biol.*, 1904, 45, 532—539).—A large number of analyses of the ash in various food-stuffs show that potassium, magnesium, and phosphoric acid are more abundant in most foods than in milk. Calcium, on the other hand, is most abundant in milk; the poverty of milk in iron is well known. For dietetic purposes, it is essential that such facts should be known. The way in which iron and calcium are combined is also important; there is some question whether inorganic iron is

absorbed, and the calcium salts of ordinary water do not appear to be assimilable. The calcium in combination with caseinogen is easily displaced by dilute acetic acid in the cold; that combined with the other proteids is small in amount, and so loosely combined that it is displaced by a soluble oxalate. Lactose and citric acid perhaps assist the solution of calcium phosphate; the amounts of citric acid and calcium appear to be proportional. W. D. H.

Condition of the Body Proteid in Inanition. EMIL ABDERHALDEN, PETER BERGELL, and THEODOR DÖRPINGHAUS (*Zeit. physiol. Chem.*, 1904, 41, 153—156).—The yield of the proteids of the blood and body generally of mono-amino-acids was investigated by the ester method in animals in health and after inanition. No difference was found in the two cases. W. D. H.

Sugar Formation in the Liver. JOSEF SEEGEN (*Chem. Centr.*, 1904, i, 195; from *Arch. Anat. Physiol., Physiol. Abth.*, 1903, 425—437).—As the sugar (dextrose) increases in the liver after removal from the body, the amount of glycogen falls, but not proportionately. In pieces of liver treated with alcohol (20—150 c.c. of absolute alcohol to 30 grams of finely-divided liver), sugar formation not only goes on, but more is formed than in pieces simply exposed to the air. W. D. H.

Action of [Pilocarpine and Adrenaline (Epinephrine)] on the Hepatic Glycogen. MAURICE DOYON and KAREFF (*Compt. rend.*, 1904, 138, 170—171).—After injection of pilocarpine hydrochloride into an intestinal vein of the dog, the glycogen in the liver diminishes or disappears; at the same time, the dextrose of the blood increases. Adrenaline has a similar effect. W. D. H.

The Simultaneous Existence in the Living Cell of Oxidising and Reducing Diastases; the Oxidising Property of Reductases. M. EMMANUEL POZZI-ESCOT (*Compt. rend.*, 1904, 138, 511).—The author claims that the results obtained by Abelous and Aloy (compare Abstr., 1903, ii, 560; this vol., ii, 188) merely confirm his previous work (compare Abstr., 1902, i, 513, 580, 654, 655; ii, 635; 1903, i, 670). M. A. W.

Alcoholic Fermentation in Animal Tissues. JULIUS STOKLASA, F. ČERNÝ, JOH. JELÍNEK, EUGEN SIMÁČEK and EUGEN VÍTEK (*Pflüger's Archiv*, 1904, 101, 311—339).—The presence of minute amounts of alcohol in animal tissues, blood, and organs has been frequently noted. Details are given of alcohol formation when various tissues are added to dextrose solution. This property depends on an enzyme and is not due to micro-organisms. W. D. H.

Influence of Electrolytes on Muscular Tone. WILLIAM D. ZOETHOUT (*Amer. J. Physiol.*, 1904, 10, 372—377).—A full account of experiments previously published (this vol., ii, 190). W. D. H.

Influence of Veratrine and Glycerol on Muscular Contraction. ADALBERT GREGOR (*Pflüger's Archiv*, 1904, 101, 71—102).—The main effect of veratrine on the muscle curve is a great prolongation of the relaxation period. Glycerol produces a very similar effect, as has already been pointed out by Langendorff and Lyle. Details of numerous experiments illustrated by reproductions of muscle curves are given. W. D. H.

Relation of Ions to Ciliary Movement. RALPH S. LILLIE (*Amer. J. Physiol.*, 1904, 10, 419—443).—Pure solutions of sodium salts destroy cilia, but potassium and ammonium salts allow movement to continue for some time. The action of sodium salts is not prevented by addition of other anions. The majority of cations exhibit antitoxic action, that is, enable movement to continue; this efficiency varies with the valency. The heavy metal cations exhibit varying antitoxic efficiency, but the order appears to be that of the metals in the solution—tension scale. In dilutions of $N/6400$ to $N/12800$, the H ion exhibits well-marked antitoxic action. The quantity of a given cation required to counteract the toxicity of a salt increases rapidly with an increase in the valency of the anion of that salt. W. D. H.

Decomposition of the Nitrogenous Substances in Ascaris. ERNST WEINLAND (*Zeit. Biol.*, 1904, 45, 517—531. Compare Abstr., 1902, ii, 155, 412).—In fasting ascarides, the nitrogen excreted per diem is 15—20 mg. for every 100 grams of body-weight. If more nitrogen is found in the surrounding water, it leads to maceration of the animal. The nitrogen is excreted as ammonia and ammonia derivatives, not as nitrates, nitrites, or free nitrogen. W. D. H.

Influence of Hydroxyl and Hydrogen Ions on the Regeneration and Growth of Tubularia. JACQUES LOEB (*Pflüger's Archiv*, 1904, 101, 340—348).—In a neutral solution of sodium chloride, potassium chloride, calcium chloride, and magnesium chloride in the proportion in which these salts occur in sea water, the regeneration of amputated *Tubularia* polyps occurs more slowly than in sea water. The same is true for growth. If a small amount of sodium hydrogen carbonate or disodium hydrogen phosphate is added to the solution, the rate is increased to that in sea water. A small amount of sodium hydroxide has a similar, but smaller and stimulating effect, showing that during growth an acid is formed which inhibits growth. Certain algæ under the influence of light excrete alkaline substances which neutralise the acid in normal sea water. W. D. H.

Effects of Salts on Kidney Excretion and Glycosuria. ORVILLE H. BROWN (*Amer. J. Physiol.*, 1904, 10, 378—383).—Certain salts (sodium chloride, citrate, acetate, &c.) produce not only diuresis, but glycosuria also. The latter is prevented by small amounts of calcium or strontium chloride; these salts also decrease or inhibit phloridzin glycosuria. The salts that produce diuresis and glycosuria are also those that stimulate nerve. Anions stimulate and cations depress renal activity. W. D. H.

Kidney Functions. II. Phloridzin Diuresis. OTTO LOEWI (*Chem. Centr.*, 1904, i, 398—399; from *Arch. exp. Path. Pharm.*, 50, 326—331).—Phloridzin causes great diuresis, but no increase in sodium chloride excretion; injection of dextrose increases the amount both of urine and sodium chloride. Phloridzin is regarded as an "indirect diuretic"; the sugar which passes into the urinary tubules hindering subsequent reabsorption of water. W. D. H.

Proteid Excretion through the Bile. AUGUST GÜRBER and B. HALLAUER (*Zeit. Biol.*, 1904, 45, 372—379).—The non-appearance in the urine of foreign proteids injected into the blood-stream is no proof that the proteid has been wholly or in part assimilated by the organism; the bile is a possible channel of excretion also. The neglect to examine the bile in most previous experiments of the kind renders a repetition of such work necessary. In the present experiments with casein, one third of the quantity injected was regained in the urine and bile; the excretion is, however, slow, and by prolonging the period of observation, it is probable that in time all the casein injected would have been recovered. There is no evidence that it is directly utilised by the body. W. D. H.

Absorption and Excretion of Certain Guaiacol Derivatives. TH. KNAPP and F. SUTER (*Chem. Centr.*, 1904, i, 391—392; from *Arch. exp. Path. Pharm.*, 50, 332—352).—The absorption of various guaiacol derivatives used in therapeutics appears to be good. The greater part is excreted in the urine as compounds with glycuronic acid. W. D. H.

Electrical Conductivity of Urine in Relation to its Chemical Composition. JOHN H. LONG (*J. Amer. Chem. Soc.*, 1904, 26, 93—105).—It has been shown previously (*Abstr.*, 1903, ii, 165) that the conductivity of urine due to metabolic products can be found by subtracting the conductivity due to the sodium chloride from the observed conductivity of the urine. Owing, however, to the fact that the conductivity of a pure aqueous solution of sodium chloride in absence of other salts is greater than the conductivity of the salt as it exists in the urine, a number of experiments have been carried out in order to ascertain the effect of other substances, namely, urea, ammonium sulphate, and disodium hydrogen phosphate, on the conductivity of sodium chloride solutions. The results of this investigation show that the conductivity of the constituents of urine other than sodium chloride may be found by diminishing the conductivity of a solution of sodium chloride of the same strength as that of the urine by about 3 per cent., and subtracting this corrected salt conductivity from the observed urine conductivity. E. G.

Urea and Urein. WM. OVID MOOR (*Zeit. Biol.*, 1904, 45, 420—463; 540—541. Compare this vol., ii, 192).—A full presentation of the author's much criticised views. W. D. H.

Nutrition Studies. IV. Composition and Energy Value of Flesh Faeces. JOHANNES FRENTZEL and MAX SCHREUER (*Chem. Centr.*, 1904, i, 199—200; from *Arch. Anat. Physiol., Physiol. Abth.*, 1903, 460—479. Compare Abstr., 1901, ii, 609; 1902, ii, 216, 514).—In three dogs on a meat diet, the nitrogen in the faeces was 8.6 to 10.6, fat from 10.1 to 13.2, and ash from 14.1 to 22.1 per cent. In addition to undigested material, considerable amounts of residues from bile and mucous membranes are present. Full analytical details with estimation of heat values are given. W. D. H.

Alloxuric Bases in Aseptic Fevers. ARTHUR R. MANDEL (*Amer. J. Physiol.*, 1904, 10, 452—457).—In various surgical cases, fever occurs after an operation, although precautions to exclude infection are taken. The blood shows leucocytosis; the alloxuric bases and the uric acid in the urine vary inversely. A large excretion of alloxuric bases, presumably from the leucocytes, is accompanied by rise of body temperature. Injection of purine bases in men and monkeys causes fever. W. D. H.

[Acetone and Diabetes.] H. CHRISTIAN GEELMUYDEN (*Zeit. physiol. Chem.*, 1904, 41, 128—152).—Acetone production is regarded not so much as a perverted form of metabolism, as an exaggeration of a normal process. The blood of diabetic men and animals contains or yields much more acetone than in health. The same is true for various organs investigated; among the organs, the liver yields comparatively small amounts. The urine contains a much higher percentage than the blood. The main cause of increase in acetone is held to be carbohydrate inanition. In ordinary circumstances, acetone and carbohydrate enter into synthetical union. In fat metabolism, two main sets of intermediate products are formed, namely, carbohydrates and substances yielding acetone. Under normal conditions, the two antagonise each other. W. D. H.

Relations between the Molecular Weight and the Physiological Action of the Higher Fatty Acids. I. Myristic and Lauric Acids. LUDWIG F. MEYER (*Zeit. physiol. Chem.*, 1904, 40, 550—564).—These two acids, when given to dogs, are well absorbed; their soaps are found in small amount only in the faeces. They are true nutriments, and exercise a proteid-sparing influence, although not so fully as their higher analogues, the customary fatty acids (palmitic, oleic, stearic). The administration of benzene increases proteid katabolism. W. D. H.

Action of Anethole on the Organism. EUGÈNE VARENNE, J. ROUSSEL, and L. GODEFROY (*Compt. rend.*, 1903, 137, 1294—1296).—Anethole is not toxic, and it is probable that this substance will take its place as a therapeutic agent. W. D. H.

Action of Codeine. JACOB BOUMA (*Chem. Centr.*, 1904, i, 393; from *Arch. exp. Path. Pharm.*, 50, 353—360).—Daily injections of 0.2 to 0.4 gram of codeine phosphate for a long time were in dogs

excreted in great measure unchanged, from 77 to 89 per cent. being recovered in urine and fæces. The organism does not possess the power of destroying the alkaloid, and no habituation to its use is set up.

W. D. H.

The Effect of Phosphorus and Arsenic Poisoning on the Bile. ALFONS PILZECKER (*Zeit. physiol. Chem.*, 1904, 41, 157—175).—The bile was collected from a fistula in dogs. Both poisons are alike in producing the appearance of epithelial elements and a considerable quantity of albumin in the bile. The total amount of bile secreted is greater with phosphorus than with arsenic. Tables are given showing other less important changes in specific gravity, viscosity, colour, &c.

W. D. H.

Effect of Poisons after Adrenaline [Epinephrine] Injections. ALFRED EXNER (*Chem. Centr.*, 1904, i, 393; from *Arch. exp. Path. Pharm.*, 50, 313—318).—After adrenaline is given intraperitoneally, strychnine and physostigmine produce toxic effects and death more slowly than in normal animals. This is attributed to the power adrenaline has of lessening the absorptive power of the alimentary tract. Subcutaneous injections of adrenaline led to inconclusive results.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Growth of Bacteria in Salt Solutions of High Concentration. FELIX LEWANDOWSKY (*Arch. Hygiene*, 1904, 49, 47—61).—In the case of sodium chloride, the most concentrated solutions in which growth of bacteria took place contained 25 per cent. (= 4.3 mols.). Potassium salts have less effect, growth being very active in broth solutions saturated with potassium nitrate. This result accords with the very slight disinfecting power of potassium nitrate observed by Patterson.

Comparing relations of equal molecular concentrations, the results show that sodium salts act somewhat more strongly than potassium salts.

N. H. J. M.

Production of Acetylmethylcarbinol by the Bacteria of the Group *Bacillus Mesentericus*. HENRI DESMOTS (*Compt. rend.*, 1904, 138, 581—583).—The following bacilli, *Bacillus mesentericus vulgatus*, *B. fuscus*, *B. flavus*, *B. niji* and *B. ruber*, were found to attack solutions of glycerol, mannitol, dextrose, sucrose, dextrin, inulin, and starch. Acetic acid, valeric acid, and small quantities of ethyl alcohol were produced in every case. By distilling the product, a laevorotatory solution was obtained which reduces Fehling's solution at the ordinary temperature and with excess of phenylhydrazine acetate

gives a precipitate of the osazone of acetylmethylcarbinol. This osazone forms pale yellow, fern-like crystals melting at 243°.

S. S.

Chemistry of the Tubercle Bacillus. WILLIAM BULLOCH and J. J. R. MACLEOD (*J. Hygiene*, 1904, 4, 1—10).—On extraction with ether, dried tubercle bacilli yield large percentages of fatty substances. On filtering the boiling extracts, a white precipitate deposits on cooling. After saponification of the filtrate with sodium hydroxide, two extracts, aqueous and ethereal, are obtainable; the latter contains some fats; the fatty acids are probably oleic, isocetic, and myristic. The aqueous extract contains a soap, the fatty acid of which corresponds in melting point with lauric acid. The filtrates also contain lipochromes. The white precipitate mentioned above can be saponified with difficulty by means of alcoholic potash; a white powder which is an alcohol is deposited, and the filtrate contains fatty acids.

W. D. H.

Two New Fluorescent Denitrification Bacteria. HARALD R. CHRISTENSEN (*Centr. Bakt. Par.*, 1903, 11, 190).—A description of two new organisms, *Bacillus denitrificans fluorescens* a, and *Bacillus denitrificans fluorescens* b.

A. McK.

Decomposition of Formic Acid by Micro-organisms. V. OMELIANSKY (*Centr. Bakt. Par.*, 1903, ii, 177—189, 256—259, 317—327).—*Bacillus formicicum*, isolated from the excrement of horses, has the property of fermenting a 2 per cent. solution of calcium formate containing 0.2 per cent. of peptone, the conditions being aerobic. Calcium formate is more suitable than sodium formate, since calcium carbonate is a product of the decomposition, thus, $\text{Ca}(\text{CO}_2\text{H})_2 + \text{H}_2\text{O} = \text{CaCO}_3 + \text{CO}_2 + 2\text{H}_2$; further, by the use of calcium formate, the solution does not become alkaline, as is the case when sodium formate is used. The temperature was maintained at 35° and the growth extended over 1 to 2 weeks. *Bacillus formicicum* is described. The formic acid taken was not all attacked. The volatile acid in the mixture after the bacterial growth consisted almost entirely of formic acid together with a little acetic acid. The gases obtained by use of a culture of *B. formicicum* consisted of about 25.2 per cent. of carbon dioxide and 74.9 per cent. of hydrogen.

B. formicicum did not flourish when inoculated into solutions of acetic, propionic, and *n*-butyric acids respectively. Growth occurred in solutions of dextrose, galactose, lactose, mannitol, dulcitol, arabinose, and maltose, whilst none occurred with sucrose, starch, dextrin, inulin, gum-arabic, ethylene glycol, glycerol, and erythritol, the results being identical no matter whether the conditions were aerobic or anaerobic.

B. formicicum differs from *Bacillus methylicus*, with which it is morphologically similar, in not flourishing in a 0.5 per cent. aqueous solution of methyl alcohol.

The author has studied the action of *B. formicicum* on mannitol and contrasts his results with those of Frankland, Stanley, and Frew on the fermentation of mannitol with *Friedländer's Pneumococcus*

(Trans., 1891, 59, 253) and those of Frankland and Lumsden with *Bacillus ethaceticus* (Trans., 1891, 60, 432). The products obtained were: hydrogen, 1.2; carbon dioxide, 30.4; ethyl alcohol, 18.5; formic acid, 0.7, acetic acid, 3.8; and lactic acid, 45.4 per cent., the latter yielding a zinc salt with $[\alpha] + 6.3^\circ$ ($c = 5.5$). [The nature of the light employed is not mentioned.] When mannitol was fermented by *B. formicicum* in a 0.1 per cent. peptone solution, *i*-lactic acid was obtained instead of *l*-lactic acid; the yield of the lactic acid was in this case small, but a considerable amount of succinic acid was detected. The products obtained from dulcitol consisted of hydrogen, 1; carbon dioxide, 30.5; acetic acid, 11.2; formic acid, 0.5; *l*-lactic acid, 25.8; succinic acid (by difference), 31.0 per cent.; dextrose yielded *l*-lactic acid, whilst lactose yielded *i*-lactic acid. A. McK.

Separation of the Hydrogen Fermentation from the Methane Fermentation of Cellulose. V. OMELIANSKY (*Centr. Bakt. Par.*, 1904, 11, 369—377. Compare Abstr., 1902, ii, 468).—Experiments are quoted on the fermentation of cellulose by the bacilli previously described. The separation of the hydrogen from the methane fermentation depends on the fact that the latter takes place at first when the culture is added; when the culture is, however, heated to 75° , the hydrogen fermentation takes place instead.

A. McK.

The Ferment present in "Harsh" or "Turned" Wine. J. B. VINCENT LABORDE (*Compt. rend.*, 1904, 138, 228—231).—In a previous communication (compare *Compt. rend.*, 1898, 126, 1223), the author had shown that the ferments which cause the "turning" of wine are analogous to the mannitic ferment of Gayon and Dubourg (compare Abstr., 1900, i, 784). Comparative experiments on the fermentative action of pure cultures of (1) Gayon and Dubourg's mannitic ferment, (2) the ferment from "turned" wine, (3) a ferment isolated from "turned" bottled wine, on sterilised white and red new wines, showed (1) that each of the three ferments had turned the wines, but that the action had proceeded much further in the case of the red than the white wine, and (2) that the third ferment was the most effective of the three as determined by the complete disappearance of the reducing sugar, and the large proportion of volatile acids (acetic and propionic) in the resulting product. The action of the three ferments on a solution of dextrose is identical, but they show a difference in their behaviour towards a solution of lævulose, the amount of mannitol formed being much less in the case of the third ferment than in the other two. M. A. W.

Yeast. J. J. VAN HEST (*Chem. Centr.*, 1904, i, 394—395; from *Zeit. ges. Brauw.*, 26, 701—706).—The paper treats of the influence yeast has on the nitrogen of the wort (which is *nil* unless the yeast cells die), and of the influence of temperature, oxygen, and attenuation through several generations on the production of zymase.

W. D. H.

Action of Sodium Fluoride on Yeast. MAURICE ARTHUS and JEAN GAVELLE (*Compt. rend. Soc. Biol.*, 1903, 55, 1481—1483).—Yeast in sugar solution is killed by sodium fluoride of one per cent. strength. Some cells resist longer than others, but their activity is lessened. W. D. H.

Influence of Strong Salt Solutions on the Force and Energy of Fermentation. ALB. J. J. VANDEVELDE (*Chem. Centr.*, 1904, i, 527—528; from *Handel. Vlaamsch. Natuur. en Geneeskundig Congres, Gent*, 27 Sept., 1903).—It has been shown (*Bull. Assoc. Belg. Chim.*, 16, 374) that strong solutions of non-poisonous salts have no influence on the fermenting force, that is, on the total quantity of carbon dioxide liberated by fermentation under certain conditions. The effect of such solutions on the energy of fermentation has been investigated in reference to temperature and the species of yeast. The energy of fermentation is defined as the number of hours required to convert three-quarters of the whole quantity of sugar into alcohol and carbon dioxide. The energy, like the force of fermentation, is independent of the osmotic pressure and concentration in the case of solutions of barium chloride, ammonium sulphate, magnesium sulphate, and zinc sulphate. There is also no relationship between osmotic pressure and energy of fermentation for solutions of potassium chloride, strontium chloride, potassium nitrate, sodium nitrate, ammonium nitrate, calcium nitrate, strontium nitrate, potassium phosphate, and ammonium phosphate, but with very concentrated solutions the energy decreases, but not proportionately to the concentration. The energy of fermentation appears to be connected with the osmotic pressure of solutions of sodium chlorate, ammonium chloride, calcium chloride, magnesium chloride, and magnesium nitrate, but varies in a very irregular manner. The influence of the salts does not appear to be of a physiological nature; they probably act more strongly on the zymase than on the yeast cells themselves. E. W. W.

Influence of Radium Rays on the Development and Growth of Lower Fungi. J. DAUPHIN (*Compt. rend.*, 1904, 138, 154—156).—Radium rays check the growth of the mycelium of *Mortierella*, and prevent the germination of the spores. The latter are, however, not killed, and germinate when again placed under normal conditions.

N. H. J. M.

Occurrence of Crenothrix Polyspora in Well Waters. ADOLF BEYTHIEN, HANS HEMPEL, and L. KRAFT (*Zeit. Nahr. Genussm.*, 1904, 7, 215—221).—The authors do not consider that the growth of *Crenothrix polyspora* depends on the ferruginous character of the water (Abstr., 1904, ii, 90), and show that some waters which are free from *Crenothrix* contain as much iron and organic matter as do other waters in which the algæ thrive. The growth appears to be more closely related to the amount of manganese salts in the water. In the analyses given, Knorre's method (Abstr., 1903, ii, 760) for estimating small quantities of manganese was employed. W. P. S.

Lipase in Cultures of Sterigmatocystis (Aspergillus). CHARLES GARNIER (*Compt. rend. Soc. Biol.*, 1903, 55, 1490—1492, 1583—1584).—Experiments are given which show the presence, illustrate the activity, and suggest the function in metabolic activity of lipase in certain fungi. W. D. H.

Assimilation of Alcohols and Aldehydes by Sterigmatocystis [Aspergillus] Nigra. HENRI COUPIN (*Compt. rend.*, 1904, 138, 389—391).—Of the different substances employed, only ethyl alcohol, glycerol, erythritol, and mannitol are assimilable. Methyl alcohol and ethylene glycol are indifferent, amyl and allyl alcohols are slightly toxic, whilst propyl and amyl alcohols and phenol are distinctly toxic.

Formaldehyde, acetaldehyde, and benzaldehyde are non-assimilable or toxic. N. H. J. M.

Proteolytic Enzyme in Germinating Barley. FR. WEIS (*Chem. Centr.*, 1904, i, 385—386; from *Zeit. Ges. Brauw.*, 26, 476—480, 497—500, 510—513, 539—542, 555—559, 587—591, 612—616, 630—633, 735—739, 791—795, 814—818, 834—838, 853—858, and 874—876. Compare Abstr., 1901, ii, 69).—Aqueous extracts of germinating barley contain two enzymes, probably peptase and tryptase, the action of which is retarded by thymol, chloroform, formol, benzoic acid, and salicylic acid. The peptic enzyme seems to be the less sensitive, at any rate, towards formol. Toluene has little effect on either. When the extract is precipitated with alcohol, the tryptic ferment is suppressed. The enzymes are almost equally soluble in water, dilute lactic acid, and glycerol, diffuse only slightly through animal membranes, and when dried withstand a temperature of at least 60°. Solutions are destroyed at about 70°. The tryptic, and probably the peptic, enzyme is not destroyed by freezing the malt extract. Light has very little effect, but the enzymes are very sensitive towards acids and alkalis. They are best preserved with toluene.

Tryptase acts on the following substances: malt, rye, and barley protein, casein, oat and wheat protein and legumin, the action increasing in degree in the order given. Egg albumin is very little changed by either enzyme.

Barley grain (not germinated) showed a very slight peptic, and no tryptic, action. The enzyme action appeared suddenly on the fourth day of germination and reached a maximum on the sixth day.

N. H. J. M.

Plants containing in their Seeds an Enzyme which Decomposes Fats into Glycerol and Fatty Acids. SERGIUS FORIN (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 1197—1204. Compare this vol., ii, 199).—The author has examined the seeds of 66 different plants, belonging to 31 families, for the presence of a fat-splitting enzyme. Such an enzyme occurs in the seeds of celandine and flax, and possibly of all plants of the genus *Linaria*. A table is given showing the percentage of oil contained in the seeds of *Xanthium strumarium*, *Tilia parvifolia*, *Delphinium elatum*, *Evonymus verrucosus*, *Galeopsis ladanum*, and *Leonurus cardiaca*, and the constants of the different oils. The

seeds of *Evonymus verrucosus* contain 43·64 per cent. of an oil, the constants of which, with the exception of the Reichert-Meissl number, are very nearly identical with those of sesamé oil.

The author concludes that the presence of the fat-splitting enzyme cannot be regarded as a characteristic of any particular family of plants.

T. H. P.

Intramolecular Respiration in Higher Plants. A. J. NABOKICH (*Chem. Centr.*, 1904, i, 194; from *Ber. deut. bot. Ges.*, 21, 467—476).—As regards the intramolecular respiration of seeds which do not contain fermentable carbohydrates, and the effect of non-fermentable substances such as peptose, asparagine, and organic acids, &c., it was found that two modifications exist. Pure alcoholic fermentation takes place in dextrose cultures and partially in mannitol, the relation of carbon dioxide to alcohol being 100 : 104·4. Organic acids are found in small quantity. Alcoholic fermentation with utilisation of organic acids was found to take place when the seeds suffered from want of fermentable carbohydrates. The utilisation of organic acid was very decided in the case of lactic acid cultures.

Peptone was very favourable to intramolecular respiration.

N. H. J. M.

Stimulants of Plant Growth and their Practical Employment. OSCAR LOEW (*Bied. Centr.*, 1904, 33, 91—94; from *Landw. Jahrb.*, 1903, 32, 437. Compare *Abstr.*, 1903, ii, 322 and 323).—Small amounts of manganese sulphate increased the yield, provided that the manuring was normal, the effect varying with different families of plants. Cruciferous plants seem to be much more sensitive than *Gramineæ*. In the case of rice, the relation of grain to straw was improved by manganese in addition to the yield being increased.

Uranyl nitrate increased the yield both of oats and of peas. Similar results were obtained with sodium fluoride and potassium iodide. Iron sulphate had a slight effect on oats.

The seeds of stimulated plants were in every respect normal.

N. H. J. M.

Emission of Water by Plants and their Spontaneous Desiccation. MARCELLIN BERTHELOT (*Compt. rend.*, 1904, 138, 16—29).—The loss of water was determined at intervals in the separated green parts and roots of *Festuca*, in the entire plant freed from soil, in the entire plant with soil, and in a sample of the soil alone.

The spontaneous drying at the ordinary temperature was complete in a few days, and followed a law of proportionality to the weight of expressible water which remained at each instant in the plant. A certain amount of water remains which can only be expelled at a higher temperature. The water which is given off at the ordinary temperature cannot be restored by contact of the plant with moist air, but only (if the drying has not gone too far) by the application of water or contact with air saturated with moisture.

N. H. J. M.

Storage of Nitrates in Plants. N. K. NEDOKUCHAEFF (*Chem. Centr.*, 1904, i, 193—194; from *Ber. deut. bot. Ges.*, 1903, 21, 431—435).—The amounts of nitrates stored by seedlings of *Helianthus annuus*, *Cucurbita Pepo*, *Phaseolus multiflorus*, and *Zea Mays*, grown in Knop's solution with different amounts of nitrate, varied according to the species and with the concentration of the solution. The accumulation of nitrates increases with the strength of the solution up to a certain point, which varies with different plants. The amount taken up also depends on the base, being greatest in presence of potassium nitrate. Any potassium salt will increase the amount of nitrates in the plants.

Plants in an atmosphere saturated with moisture take up less nitrate, and smaller amounts are stored by etiolated plants than in presence of light. N. H. J. M.

The Entrance of Metallic Elements in Plants. OSCAR LOEW (*Pflüger's Archiv*, 1903, 100, 335—336).—Bokorny showed that in plant life the place of one element cannot be taken by another. This rule is confirmed, but has one exception; in some lower fungi, rubidium can take the place of potassium. W. D. H.

Normal Occurrence of Salicylic Acid in Certain Plants of the Violaceæ. ALBERT DESMOULIÈRE (*J. Pharm. Chim.*, 1904, [vi], 19, 121—125. Compare Abstr., 1902, ii, 40).—Many plants of this order yield methyl salicylate, which probably results from the hydrolysis of a glucoside analogous to gaultherin, on distillation in a current of steam. The glucoside has not, however, been obtained in a crystalline form. Cherries contain salicylic acid in amounts varying from 0.1 to 0.21 mg. per kilo., and the acid is present in *Calendula officinalis* to the extent of 0.43 mg. per kilo. G. D. L.

Hexone Bases in the Tubers of Potatoes and Dahlia. ERNST SCHULZE (*Landw. Versuchs-Stat.*, 1904, 59, 331—343).—Both histidine and lysine occur in potato tubers, and arginine in potatoes and dahlia. This lends support to the view that the mixture of crystallising nitrogenous substances present in roots and tubers is very similar in composition to that found in etiolated seedlings. N. H. J. M.

Formation of Terpenic Compounds in Chlorophyll Organs. EUGÈNE CHARABOT and ALEXANDRE HÉBERT (*Compt. rend.*, 1904, 138, 380—381).—The suppression of inflorescence resulted in an increased production of stem (of peppermint) and an increase in the amount of essence (both per cent. and actual) in the green portions. The terpenic compounds are therefore produced by the chlorophyll organs. In absence of light, the production is greatly reduced. N. H. J. M.

Effect of Oil of Turpentine on the Changes in the Proteids in Plants. MARIE LESCHTSCH (*Chem. Centr.*, 1904, i, 194—195; from *Ber. deut. bot. Ges.*, 21, 425—431).—The production of proteids in wounded bulbs of *Allium cepa* and *A. ascalonium* was increased by small amounts of turpentine vapour, but hindered by large amounts.

Entire bulbs were not affected. In wheat seedlings, the decomposition of proteids was perceptibly checked by oil of turpentine. Both the bulbs and the seedlings are killed by large amounts of oil of turpentine.

N. H. J. M.

Existence in Plants of an Oxidising-reducing Diastase. J. E. ABELOUS and JULES ALOY (*Compt. rend.*, 1904, 138, 382—384).—It was found that vegetable sap contains an oxidising-reducing diastase similar to that found in animal organs (Abstr., 1903, ii, 560; this vol., ii, 188). In the case of plants, however, the activity of the ferment is suppressed by oxydases of the laccase type. The oxidising action may be shown by adding potassium chlorate, for example.

N. H. J. M.

Composition of the Fatty Oil of *Aspidium Spinulosum*. P. FARUP (*Arch. Pharm.*, 1904, 242, 17—24).—The oil was prepared by extracting with ether a powder which had been left after an extract of the rhizomes had been mixed with calcined magnesia and extracted with water, to remove filicic acid and allied substances. It consisted mainly of olein. In addition to oleic acid and glycerol, phytosterols, linolic acid (forming about 4 per cent. of the liquid acids), solid fatty acids (in amount too small to admit of separation), a little butyric acid, and probably isolinolenic acid were detected. The liquid acids were detected by dissolving the mixture of them in aqueous potassium hydroxide, oxidising the solution with potassium permanganate in the cold, and identifying the hydroxy-acids formed. Katz (Abstr., 1899, ii, 324) did not find phytosterol in *Aspidium Filix mas*. C. F. B.

Toxicology of *Agaricus Muscarius*. ERNST HARMSSEN (*Chem. Centr.*, 1904, i, 384—385; from *Arch. exp. Path. Pharm.*, 50, 361—452).—The amount of muscarin in an extract and in the original fungus can be approximately determined by the effect on frogs and cats, 0.05 mg. of the pure substance stopping the action of a frog's heart. The same effect is produced in the case of cats with half this amount. It was found that the fresh substance of the fungus contained 15 per cent. of muscarin. Poisoning by muscarin and by the fungus are, however, not identical, as the fungus contains a second poison, which is extracted by water from the residue left after extracting the muscarin with alcohol. The second poison is an unstable substance which diminishes in quantity when the fungus is dried.

N. H. J. M.

Toxic Action of Acids and Salts on Seedlings. FRANK K. CAMERON and J. F. BREAZEALE (*J. Physical Chem.*, 1904, 8, 1—13).—The concentration of solutions of various acids, potassium and calcium salts, which caused death of small seedlings of maize, wheat, and clover were determined. In the case of the latter plant, the value found was the same for all the acids, namely, $N/20000$, so that here the toxic effect appears due to the hydrogen ion. For maize, however, the values varied from $N/600$ to $N/3000$, and for wheat from $N/15000$ to $N/20000$. The concentrations required for the salts were

considerably higher, varying from about $N/100$ for potassium carbonate to about $N/5$ for calcium chloride. Addition of potassium salt was found also to decrease the toxic effect of the acids on maize and wheat, but apparently increases its effect on clover; calcium salts, however, decrease the toxic effect of acids on all the seedlings. Although the author does not consider the results are opposed to the dissociation theory, yet they make it evident that toxic effect cannot be regarded as simply an ionic property.

L. M. J.

The Carbohydrates of Barley and their Changes during Germination. LÉON LINDET (*Chem. Centr.*, 1904, i, 383—384; from *Ann. Brass. Dist.*, 1903, 289—295, and *Zeit. ges. Brauw.*, 26, 641—645).—Barley contains amylan and galactan besides sucrose and dextrose. During germination, the galactan and sucrose increase, the latter yielding invert sugar, of which the lævulose is more rapidly utilised than the dextrose, especially at the commencement of germination. Maltose or dextrin are never found. The starch is converted into sucrose, either directly or with production of maltose (Brown and Morris), as unstable intermediate product. Conversion of sucrose into starch was often established.

It is uncertain whether galactan is formed from starch; it is certainly not derived from cellulose.

N. H. J. M.

Pentosans as Constituents of Foods, especially Rye Straw. ALBIN VON RUDNO RUDZINSKI (*Zeit. physiol. Chem.*, 1903—1904, 40, 317—390).—The results of experiments with rye showed that the various manures employed had no effect on the percentage of pentosans in the straw. The amount in the dry matter of the straw was 27.07—27.92 per cent. The pentosans vary in quantity in the different parts of the straw, being lowest (26.52 per cent.) in the lowest third and increasing upwards; the ear spindles contained 33.03 per cent.

As regards the digestibility of the pentosans of rye straw fed in conjunction with moderate amounts of readily soluble carbohydrate, it was found that sheep digested 46.66—46.99 per cent. The digestibility was increased (to 70.2 per cent.) by digesting the straw with water (three parts) containing sodium hydroxide (3—4 per cent. of the weight of the straw) for 6 hours under 6 atmospheric pressures (Lehmann, *Deut. landw. Presse*, 29, 445).

In presence of excessive amounts of readily soluble carbohydrates, the digestibility of the pentosans was much diminished, but not to the same extent as that of the crude fibre.

N. H. J. M.

Pot Experiments on the Effect of Liming and Marling on the Yield of Serradella RICHARD ULBRICHT (*Landw. Versuchs-Stat.*, 1904, 59, 425—432. Compare *Abstr.*, 1903, ii, 240).—The greatest yield was obtained after applying a very small amount of nitrogen, together with phosphoric acid and potassium, notwithstanding the small amount of lime in the soil. Lime, marl, and even limestone meal diminished the yield, but the effect of lime was much the greatest.

The injurious effect of exclusive application of marl to soil deficient in all manurial constituents, previously observed in the case of vetches, was also noticed in the experiments on serradella.

N. H. J. M.

Manurial Experiments with Tobacco. MAX LEHMANN and S. TOBATA (*Landw. Versuchs-Stat.*, 1904, 59, 443—472. Compare Abstr., 1903, ii, 681).—A number of pot experiments on the effect of various manures on tobacco grown in Japanese soils are described. Both wood ash and straw ash gave good results and acted favourably on the burning qualities of the tobacco. Soy bean meal also gave good results, being at least equal to rape cake, although the percentage of water in the beans was somewhat increased. Sodium nitrate had a similar effect. Fish guano injured the quality of the tobacco.

N. H. J. M.

Influence of Soil Moisture on the Composition of Certain Plant Parts. JOHN A. WIDTSON (*J. Amer. Chem. Soc.*, 1903, 25, 1234—1243).—The composition of plants and of parts of plants is greatly influenced by the amount of water in the soil, the constituents which show the greatest variations being the proteids and the non-nitrogenous extract. The proteids increase when the supply of water is diminished, whilst the non-nitrogenous extract and the fat decrease.

The following summary shows the differences between the highest and lowest percentages in dry matter, due to varying amounts of soil moisture :

| | Proteids. | Fat. | Non-nitrogenous extract. | Starch. |
|------------------|-----------|------|-----------------------------|---------|
| Maize kernels... | 2.56 | 0.90 | 2.33 | — |
| Oat „ ... | 5.31 | 0.68 | 1.69 | — |
| Wheat „ ... | 11.46 | 1.78 | 12.43 | — |
| Potatoes | 4.24 | — | 5.70 | 6.93 |
| Sugar-beet | 4.88 | — | 5.05 | — |

N. H. J. M.

Rennet Enzyme as a Cause of Chemical Changes in the Proteids of Milk and Cheese. LUCIUS L. VAN SLYKE, H. A. HARDING, and EDWIN B. HART (*J. Amer. Chem. Soc.*, 1904, 25, 1243—1256).—The results of experiments with milk and cheese showed that there was little or no proteolytic action of either rennet enzyme or commercial pepsin except in presence of acid. Paracasein monolactate is formed in milk and curd in the presence of acid, and proteolysis takes place, with the rennet ferment as the active agent. The chemical work of both rennet enzyme and commercial pepsin is chiefly confined to the production of paranuclein, caseoses, and peptones ; no ammonia is formed and only traces of amides.

In normal cheese, the amounts of amides and ammonia increase with age, whilst the compounds previously formed diminish. The first stage in normal ripening is a peptic digestion of paracasein monolactate ; then amides are gradually formed and later on ammonia.

When rennet enzyme was the only digesting agent present in cheese, no trace of cheese flavour could, in any case, be detected.

N. H. J. M.

Influence of the Carbon Dioxide of the Soil on Vegetation. EM. DEMOUSSY (*Compt. rend.*, 1904, 138, 291—293).—The results of pot experiments with lettuce showed that sterilised soil gave as good results as normal soil when the composition of the surrounding air was rendered similar, by placing sterilised and unsterilised soil under the same bell-jar, and that sand in normal air gave the same results as sterilised soil.

The conclusion is drawn that the organic matter of the soil does not directly act as plant food. It is probable that short plants are benefited by the carbon dioxide liberated from the soil.

N. H. J. M.

Distribution of Potassium in Arable Soil. J. DUMONT (*Compt. rend.*, 1904, 138, 215—217).—The amounts of potash were determined in the mechanically separated portions of Grignon soil and a granite soil from La Creuse. The following results were obtained :

| | K ₂ O per cent. in dry soil. | | Per cent of total K ₂ O. | |
|----------------|---|-----------------|-------------------------------------|-----------------|
| | Grignon soil. | La Creuse soil. | Grignon soil. | La Creuse soil. |
| Coarse sand... | 0.148 | 0.605 | 16.55 | 70.93 |
| Fine sand..... | 0.588 | 0.225 | 65.78 | 26.37 |
| Clay | 0.158 | 0.023 | 17.67 | 2.70 |

The supposition that the chemical activity of a soil depends mostly on the fine particles accords with the fact that potassium manures are generally inefficacious in the case of Grignon soils, and act favourably on the granitic soils.

N. H. J. M.

Organic Matter in Soils and Sub-soils. FRANK K. CAMERON and J. F. BREAZEALE (*J. Amer. Chem. Soc.*, 1904, 26, 29—45).—The chromic acid method is recommended for estimating carbon in soils, and it was found more convenient to include the carbon present as carbonates than to treat the soil with sulphurous acid, the carbonates being determined separately and the amounts deducted from the total carbon.

The results of a considerable number of estimations of carbon in extracted humus showed an average of 42 per cent., instead of 56 per cent., the figure adopted by Wollny, Wolf, van Bemmelen and others. It is not, however, considered desirable to make any alteration in the factor for the present.

The ash of humus was, in one case, mainly lime, but as a rule it consisted chiefly of iron oxides, alumina and silica ; manganese was, in several cases, found in considerable quantity.

N. H. J. M.

Solubility of Phosphorite under the Influence of Physiologically-acid Salts. J. W. SCHULOFF (*Bied. Centr.*, 1904, 33, 79—80 ; from *J. exper. Landw.*, 1902, 3, 711—719).—The results of

pot experiments with barley showed that much larger yields are obtained when a mixture of phosphorite and ammonium salt is used as manure, than when the two substances are separated. This is attributed to the action of the acid of the ammonium salt on the phosphorite

N. H. J. M.

Analytical Chemistry.

Apparatus for the Continuous Extraction of Liquids. ARTURO PELIZZA (*Chem. Zeit.*, 1904, 28, 186).—The solution to be extracted is introduced into *E*, and into *P* is brought a sufficiency of the solvent (ether, benzene, light petroleum). When this is boiled, it passes as vapour through the tube *V* into *E*, where it is condensed by aid of the jacket, and then collects at the top. It then runs back through the central tube into *P*, where it is again vaporised; and so the process goes on for any desired length of time. The condenser *R* completes the condensation of the vapour. The stop-cock, *r*, serves for the emptying of the apparatus and the control of the extraction process.

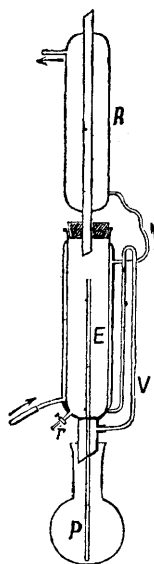
L. DE K.

Nephelometer, an Instrument for Detecting and Estimating Opalescent Precipitates. THEODORE W. RICHARDS and ROGER CLARK WELLS (*Amer. Chem. J.*, 1904, 31, 235—243).—The nephelometer was devised by Richards (*Proc. Amer. Acad.*, 1894, 30, 385) for estimating the precipitate in opalescent liquids containing not more than 0.001—0.002 gram per litre. The method depends on the fact that these finely divided precipitates reflect light, the intensity of which is a function of the quantity of the precipitate.

A modification of this apparatus is now described in which the prisms are so arranged that the images to be compared are brought side by side, and very small amounts of suspended precipitates can therefore be estimated with ease and accuracy. The chief source of error lies in the state of the precipitate, and in order to exclude variation the solution to be estimated and the standard solution for comparison should be precipitated in exactly the same way.

E. G.

New Gasvolumeter. J. GRUSZKIEWICZ (*Zeit. anal. Chem.*, 1904, 43, 85—91).—This instrument avoids the inconveniences caused by the performance of the reaction in the gas burette itself, and those resulting from the use of caoutchouc for connecting a reaction flask with the eudiometer. The general plan of the apparatus is that of



Lunge's gasvolumeter, but the reaction vessel, which consists of two concentric glass cylinders, the inner one being open at the bottom and stoppered at the top, whilst the outer one has a stop-cock at the bottom and a side burette for admitting reagents, is connected with the top of the eudiometer by a glass tube. Mercury is drawn into the reaction vessel before commencing an analysis, and the agitation of the liquids is entirely effected by raising and lowering the mercury reservoir. The apparatus can be employed for all analyses involving the measurement of a gaseous product. M. J. S.

Determination of the Reaction of a Liquid by means of Indicators. HANS FRIEDENTHAL (*Zeit. Elektrochem.*, 1904, 10, 113—119).—The "reaction" of a solution, or the concentration of the hydrogen ions in it, is determined by adding an indicator and comparing the colour produced with that given with a solution of known concentration. The following series of standard solutions is used, the concentrations being given in gram-equivalents per litre.

| Concentration of H ions. | Concentration of solution. | Concentration of H ions. | Concentration of solution. |
|--------------------------|----------------------------|--------------------------|----------------------------|
| 2 | 6.034 HCl | 1×10^{-8} | 0.000001 KOH or |
| 1 | 1.35 HCl | | 0.00204 aniline |
| 1×10^{-1} | 0.103 HCl | 1×10^{-9} | 0.00001 KOH or |
| 1×10^{-2} | 0.01007 HCl | | 0.204 aniline |
| 1×10^{-3} | 0.001 HCl | 1×10^{-10} | 0.0001 KOH |
| 1×10^{-4} | 0.0001 HCl | 1×10^{-11} | 0.001 KOH |
| 1×10^{-5} | 0.00001 HCl or | 1×10^{-12} | 0.0102 KOH |
| | 0.0588 boric acid | 1×10^{-13} | 0.104 KOH |
| 1×10^{-6} | 0.000001 HCl or | 1×10^{-14} | 1.38 KOH |
| | 0.000588 boric acid | 1×10^{-15} | 3.8 KOH |
| 1×10^{-7} | pure water | | |

The neutral solution may also be made up in a number of other ways, one of which is described later. The indicators used are given in the following list; 0.1 c.c. of a solution containing 0.01 gram molecule per litre is added to 10 c.c. of the solution to be tested and the colour compared by transmitted light with the standard solutions. Indicators suitable for the most acid solutions stand at the beginning of the list: tropaeolin, neutral-red, methyl-violet, methyl-orange, Congo-red, lacmoid, litmus, gallein, rosolic acid, *p*-nitrophenol, sodium alizarinsulphonate, neutral-red, tropaeolin, phenolphthalein, α -naphtholbenzoin, sodium alizarinsulphonate, gallein, Poirrier's blue, methyl-violet, gallein. When an indicator is mentioned twice, it indicates that it gives two changes of colour.

It is stated that acid solutions always give correct results with acid indicators and alkaline solutions with basic indicators, whereas slightly acid (or alkaline) solutions give variable results with basic (or acid) indicators owing to the formation of salts, especially when the solution contains weak electrolytes. A useful set of standard solutions for comparison with nearly neutral solutions of weak electrolytes is

obtained by mixing $N/10$ solutions of (a) Na_2HPO_4 and (b) NaH_2PO_4 ; a solution containing 2 c.c. of (a) and 8 c.c. of (b) is almost exactly neutral. These solutions are especially applicable to the determination of the reaction of the fluids contained in the animal body, several of which, previously supposed to be alkaline, are found to be almost absolutely neutral. T. E.

New Titration Apparatus. HEINRICH FRINGS (*Chem. Centr.*, 1904, i, 606—607; from *Deutsche Essig Industrie*, 8, 10—12).—A complex apparatus devised for those works where a large number of titrations of the same kind have to be performed. The main feature of novelty is that a single tap suffices for the measuring pipette, the burette, and the connection between the latter and the stock bottle.

L. DE K.

Volumetric Analysis. GEORG LUNGE (*Zeit. angew. Chem.*, 1904, 17, 195—203, 225—236, 265—270. Compare Abstr., 1903, ii, 389).—An exhaustive criticism of several volumetric methods, too lengthy for useful abstraction.

The article comprises: errors due to glass vessels; the true litre and its sub-divisions; action of caoutchouc and vaselin on iodine and permanganate; reading of burettes. *Indicators.*—Phenolphthalein; nitrophenols; iron salicylate. *Standard salts for alkalimetry and acidimetry.*—Potassium di-iodate; potassium tetraoxalate; sodium tetraoxalate; sodium carbonate. *Iodometry.*—Starch solution; comparison of sodium thiosulphate and arsenious oxide towards iodine solution; potassium di-iodate as standard salt in iodometry; standardisation of iodine with sodium sulphite. *Standard salts for checking permanganate solutions.*—Oxalic acid; oxalates; metallic iron; hydrogen peroxide. Comparison of results.

L. DE K.

Estimation of Moisture in Nitroglycerol Explosives. ARTHUR MARSHALL (*J. Soc. Chem. Ind.*, 1904, 23, 154—155).—The cordite or other explosive is ground in a small mill and that portion selected for analysis which passes through a sieve having holes of the size of No. 8 wire gauge, but not through one with holes equal to No. 14 wire gauge. Five grams of this material are placed in an aluminium dish $2\frac{1}{4}$ inches in diameter and $\frac{5}{8}$ inch in depth. The dish is surmounted by a flange or collar on which rests a glass cone $4\frac{1}{4}$ inches in height. Small spaces are left between the cone and flange for the passage of the water vapour. After weighing the whole apparatus and its contents, it is placed on a metal plate over a water-bath until all water is driven off, then cooled in a desiccator, and re-weighed. For ordinary cordite, 1 hour's heating is sufficient; but for cordite containing 65 per cent. or more of gun-cotton, 2 hours or longer are required to drive off the moisture.

W. P. S.

Estimation of Fluorine in Fluorides. A Critical Examination of the Wöhler-Frösenius Method. KARL DANIEL (*Zeit. anorg. Chem.*, 1904, 38, 257—306).—As the results of his investigations, which include a large number of actual experiments, the author comes to the conclusion that the fluorine is quantitatively converted

into silicon tetrafluoride in this method. Good results may be obtained if the conditions are adhered to. In some cases, where the excess of anhydrous silica is large, a non-volatile substance is formed to some extent.

A method is given for the detection of fluorine. The substance to be tested is mixed with quartz powder and placed in a test-tube. The latter is closed by a cork through which passes a glass rod, reaching almost to the bottom of the tube and slightly enlarged at its lower end. This knob is painted black and a drop of water is placed on it. On adding sulphuric acid and warming cautiously, a white film forms on the surface of the drop of water, should fluorine be present. The glass rod may be of such a size that it almost touches the sides of the test-tube, thereby diminishing the internal space of the latter. 0.1 mg. of fluor-spar can be detected by this test. Conversely, the test serves for the detection of silicates. It is necessary, however, to fuse the silicate with a mixture of sodium and potassium carbonates, before applying the test. The addition of a little magnesite is advisable, to give a steady evolution of carbon dioxide in the test-tube and bring the silicon tetrafluoride more rapidly in contact with the drop of water.

W. P. S.

Volumetric Estimation of Sulphurous Acid. JOHANNES PINNOW (*Zeit. anal. Chem.*, 1904, 43, 91—96).—It has been stated that a mixture of sulphite and thiosulphate can be analysed by titrating one portion with iodine and another with permanganate, on the assumption that both sulphurous and thiosulphuric acids are completely oxidised to sulphuric acid by permanganate. This is not the case. An indefinite portion, about 15 per cent., of the sulphurous acid is oxidised to dithionic acid. The oxidation proceeds somewhat further in strongly alkaline solutions, but is still incomplete. It is moreover affected by dilution. The titration of sulphurous acid by iodine is also influenced to some extent by the degree of dilution, being incomplete if the solution is too concentrated. M. J. S.

Estimation of Phosphorus in Phosphorus-oil and Similar Preparations. JULIUS KATZ (*Arch. Pharm.*, 1904, 242, 121—138).—Of the phosphorus-oil 10.0 grams are shaken vigorously with 20 c.c. of 5 per cent. aqueous copper nitrate until a permanent black emulsion is obtained. Then 50 c.c. of ether are added, and hydrogen peroxide (about 10 c.c.), little by little, with constant shaking, until the black colour has disappeared entirely. The aqueous liquid is then run off, the ether washed 3 times with 10—20 c.c. of water, and the united aqueous liquids evaporated to 10—20 c.c. on the water-bath after the addition of a few drops of hydrochloric acid. The residue is filtered from drops of oil, ammonia is added to it until the precipitate which forms at first has redissolved; the phosphoric acid is then precipitated with magnesia mixture and weighed in the usual manner.

The method is a modification of Straub's (*Abstr.*, 1903, ii, 691). The hydrogen peroxide effects a much more rapid oxidation of the black copper phosphide than air does. The ether further promotes this action, and in addition it accelerates the separation of the aqueous

layer. As the only metal present is copper, which is not precipitated by excess of ammonia, preliminary precipitation of the phosphoric acid with molybdate is unnecessary. Copper sulphate must not be used, as the precipitate is then contaminated with basic magnesium salts. Test estimations with solutions of phosphorus in olive oil and in carbon bisulphide, about 0.5 per cent. in strength, gave errors of only - 0.7 to - 1.1 per cent. of the total amount, which was 0.08—0.05 gram in each experiment.

The composition of the black precipitate of copper phosphide corresponds approximately with the formula Cu_2P_2 .

Various oils were saturated at the ordinary temperature by shaking them for 1—2 hours with liquefied phosphorus; the percentages of phosphorus then contained in them was found to be as follows: oil of almonds, 1.13; olive oil, 1.08; oil of sesame, 1.06; oil of arachis, 1.20; rape-seed oil, 1.16; cod liver oil, 1.13; oil of poppies, 1.11; linseed oil, 1.15; castor oil, 0.70; paraffin oil, 1.33.

The method cannot be used to estimate the percentage of phosphorus in an alcoholic solution, the error being - 30 per cent. or more. Saturated solutions in 90 per cent. and in absolute alcohol probably contain more than 0.1 and 0.2 per cent. of phosphorus respectively.

C. F. B.

Electrolytic Estimation of Arsenic. SAMUEL R. TROTMAN (*J. Soc. Chem. Ind.*, 1904, 23, 177—179).—The apparatus used is similar to that described by Thorpe (*Trans.*, 1903, 974). The cell employed is made of glass, with a parchment-paper diaphragm, the upper end of the cell being fitted with a rubber bung through which pass the tap, funnel, and electrode. An outer vessel of water surrounds the cell in case the diaphragm bursts. The apparatus will detect 0.000001 gram of arsenious oxide.

W. P. S.

Estimation of Arsenic in Sulphuric and Hydrochloric Acids. N. G. BLATTNER and J. BRASSEUR (*Chem. Zeit.*, 1904, 28, 211).—An application of the process devised by Seybel and Wikander (*Abstr.*, 1902, ii, 289).

Arsenic in hydrochloric acid.—Fifty c.c. of the sample, which should, if necessary, be brought to a sp. gr. of about 1.18 by judicious addition of sulphuric acid of sp. gr. 1.45, are mixed with 5 c.c. of a 30 per cent. solution of potassium iodide, and after waiting for one minute the liquid is filtered through glass wool. After washing the precipitate with a few c.c. of pure hydrochloric acid containing 10 per cent. of the potassium iodide solution, the arsenic tri-iodide is dissolved in water, and after adding a slight excess of sodium hydrogen carbonate, the arsenious acid formed is titrated as usual with *N*/10 iodine solution.

Arsenic in sulphuric acid.—The acid should first be diluted to a sp. gr. of 1.45. Twenty-five c.c. of the sample are then mixed with 25 c.c. of pure hydrochloric acid and 5 c.c. of potassium iodide solution, and further treated as above. In calculating, due allowance must be made for any dilution the samples have undergone.

T. H. W.

Volumetric Estimation of Arsenic and Antimony in Nickel Ores. H. NISSENSON and ALWIN MITTASCH (*Chem. Zeit.*, 1903, 28, 184—186).—0.5 gram of the ore is heated with 8 c.c. of strong sulphuric acid on a sand-bath for some hours until the mass has assumed a white or yellowish-white colour. It is then boiled with 100 c.c. of water and at once treated with hydrogen sulphide. The precipitate is collected and washed, and again heated with 7 c.c. of sulphuric acid for some hours until all the sulphides have dissolved. The residue is then dissolved in 100 c.c. of boiling water, and the joint arsenic and antimony titrated with $N/10$ potassium bromate, using indigo as indicator (*Abstr.*, 1903, ii, 697).

The liquid is mixed with a little more bromate solution, concentrated by evaporation, 1 gram of tartaric acid is added, then ammonia, and finally 30 c.c. of magnesia mixture. After the arsenic has precipitated, the filtrate is concentrated, acidified with sulphuric acid, and treated with hydrogen sulphide. The precipitate is washed, redissolved in hot sulphuric acid, and the resulting solution titrated with potassium bromate as already described. This gives the antimony only, and the arsenic is found by difference. The results are sufficiently accurate for technical purposes. L. DE K.

Estimation of Carbon Dioxide by Densimetry. AUGUSTUS D. WALLER and B. J. COLLINGWOOD (*Proc. physiol. Soc.*, 1903, xxxvi—xxxix; xxxix—xlii; *J. Physiol.*, 30).—With certain precautions, the method previously described by Waller for the estimation of ether and chloroform vapour in air (*Abstr.*, 1903, ii, 699) may also be employed for the estimation of carbon dioxide. The method was controlled by estimations by absorption in potash.

By making such observations with inspired and expired air, it is possible to calculate the respiratory quotient; certain fallacies in the usual method of reckoning this number are pointed out. W. D. H.

Estimation of Potash in Soils, Ashes, &c. JULIUS HASENBÄUMER (*Chem. Zeit.*, 1904, 28, 210—211).—The hydrochloric acid solution of the soil is evaporated in a porcelain dish, redissolved in water, and transferred to a platinum basin. A little ammonia and ammonium carbonate are added, and after evaporating to dryness, the residue is heated over a rose burner until the ammoniacal salts have been expelled, and the organic matter destroyed. The residue is then treated for some time with hot water, and the potassium is estimated in the filtrate as usual with platinic chloride or perchloric acid.

Should the sample contain a decided amount of sulphuric acid, this must be first removed with barium chloride. L. DE K.

Estimation of the Amount of Sodium Carbonate necessary to Precipitate Lime and Magnesia in the Chemical Purification of Water. LÉO VIGNON (*Bull. Soc. chim.*, 1904, [iii], 31, 108—110. Compare *Abstr.*, 1899, ii, 452).—When water is titrated with sodium carbonate by the process suggested by Vignon and Meunier (*loc. cit.*) at the ordinary temperature, the quantity (A) of sodium carbonate which must be added in order to produce a red coloration with phenol.

phthalein is less than the amount (*B*) required when the titration is effected by boiling the water in a nickel crucible for 30 minutes with excess of the sodium carbonate solution and then determining the unused sodium carbonate remaining. When the titration is carried out at temperatures intermediate to these and in varying periods of time, quantities intermediate in value between (*A*) and (*B*) are obtained. It is pointed out therefore that in determining the amount of sodium carbonate to be added to water as a purifying agent, the temperature at which the water is to be used and the time it will be in contact with the reagent should be taken into account. The quantity of sodium carbonate remaining in the purified water should not exceed 10 grams per cubic metre. T. A. H.

Rapid Estimation of Mercury by means of Hypophosphorous Acid. BERNARD F. HOWARD (*J. Soc. Chem. Ind.*, 1904, 23, 151—153).—From 1 to 3 grams of the mercury salt under examination are treated with from 10 to 30 c.c. of hypophosphorous acid of sp. gr. 1.136, and heated for about 20 minutes on the water-bath. The globule of mercury formed is washed with water, alcohol, and ether, all the washings being passed through a small filter which previously has been washed with hypophosphorous acid, alcohol, and ether, dried and weighed. The globule of mercury, after drying in a desiccator, is weighed, as is also the film of mercury collected on the filter. The method gives trustworthy results with most mercury salts, with the exception of mercuric iodide. In the case of mercuric nitrate, water must be added before reducing. W. P. S.

Separation of the Metals of the Ammonium Sulphide Group, especially in presence of Nickel and Cobalt. HANS BOETTCHER (*Zeit. anal. Chem.*, 1904, 43, 99—104).—The following scheme is proposed as an improvement on the ordinary method for the qualitative detection of the metals in the precipitate produced by ammonium sulphide. The precipitate is dissolved in nitrohydrochloric acid and the solution evaporated. After redissolving in dilute hydrochloric acid, an excess of sodium hydroxide and some bromine are added. The filtrate is acidified in the cold (to avoid reducing chromic acid), mixed with excess of ammonium carbonate, and boiled to precipitate alumina. The filtrate is boiled with sodium hydroxide and examined for zinc and chromic acid. The precipitate containing cobalt, nickel, iron, and manganese is dissolved in hydrochloric acid, the excess of acid expelled, and much ammonia added with a little hydrogen peroxide. Cobalt and nickel pass into solution and are separated by potassium nitrite. Iron and manganese are then separated by the basic acetate method. If phosphates are present, it is merely necessary to test for iron before the separation from manganese, and then to add a sufficiency of ferric chloride before boiling with sodium acetate. After precipitating manganese as sulphide, the alkaline earths will be found in the filtrate. M. J. S.

Preparation of Pure Iron for Standardising Permanganate. ANTON SKRABAL (*Zeit. anal. Chem.*, 1904, 43, 97—98).—Most commercial

specimens of Mohr's salt contain other metals, notably zinc, from which, owing to their double salts crystallising isomorphously with that of iron, it cannot be purified by recrystallisation. By starting with a ferric salt, the metals of the zinc group can be eliminated. Iron-ammonium alum is therefore repeatedly crystallised from an acid solution, or, still better, the iron is precipitated several times by boiling a solution nearly neutralised with ammonium carbonate. The requisite quantity of ammonium sulphate is then added, and the ferric salt reduced to ferrous salt by electrolysis, employing a large platinum foil cathode and a wire anode. The ferrous ammonium sulphate is then twice recrystallised or fractionally precipitated by alcohol, thus freeing it from metals of the aluminium group. In this way, a stock of pure Mohr's salt can be secured, from which, by the author's process (*Abstr.*, 1903, 22, 685), perfectly pure iron can at any time be obtained.

M. J. S.

Distinctive Character of the Salts of Cobalt and Nickel. GABRIEL GUÉRIN (*J. Pharm. Chim.*, 1904, [vi], 19, 139).—On adding excess of potassium hydroxide, followed by 2 per cent. solution of iodine in potassium iodide until a yellow coloration of the liquid is produced, cobalt salts give the black sesquioxide, whilst those of nickel give the green hydroxide. Similar results follow the treatment of the ferrocyanide, carbonate, and phosphate precipitates of these metals.

Potassium hydroxide alone gives black sesquioxide with the ferri-cyanides, instantly with that of nickel, and less rapidly with that of cobalt.

G. D. L.

Colour Reactions of Molybdic Acid. M. EMMANUEL POZZI-ESCOT (*Compt. rend.*, 1904, 138, 200. Compare Matignon, this vol., ii, 214).—A solution of tannin gives an orange coloration with a neutral solution of molybdic acid, which becomes cherry-red in concentrated and yellow in dilute solutions; the reaction is a very delicate one and capable of detecting 1 part of molybdic acid in 100,000 parts of a solution of the ammonium salt. The colour is destroyed by acids, but is not altered by boiling. Similar colour reactions are given by gallic acid and pyrogallol, extract of yellow-wood, and other tannifers. Extract of logwood gives a brown precipitate, but no characteristic colour. Some of these coloured molybdic compounds dye wool and leather brilliant shades. Small quantities of iron give no reaction with tannin in the presence of molybdenum.

M. A. W.

Volumetric Estimation of Tungsten-steel and Ferrotungsten. E. KUKLIN (*Chem. Centr.*, 1904, 1, 543—544; from *Stahl u. Eisen*, 24, 27).—The process is based on the fact that metatungstic acid is reduced by zinc to the dioxide, which may then be titrated with permanganate.

Tungsten-steel is dissolved in a mixture of equal parts of sulphuric and phosphoric acid diluted with treble the volume of water; the solution is oxidised with permanganate and divided into two equal parts. One half is treated with excess of zinc, and the resulting liquid is titrated with permanganate. In the other half, the iron is

estimated by means of stannous chloride and iodine, and from the result it is calculated how much permanganate this iron has reduced; the balance then represents permanganate due to oxidation of tungsten dioxide.

Ferrotungsten is fused with ammonium nitrate, the nitrates are decomposed by a strong heat, and the oxides are fused with potassium sodium carbonate. The fused mass is then treated with the above acid mixture. Ferrotungsten may also be attacked by fusion with sodium pyrosulphate. L. DE K.

Analysis of Commercial Tin; Rapid Estimation of Tungsten and Iron. LOUIS CAMPREDON and G. CAMPREDON (*Ann. Chim. anal.*, 1904, 9, 41—45).—*Lead, iron, manganese, zinc.*—Ten grams of the sample are dissolved in a mixture of 10 c.c. of nitric and 80 c.c. of hydrochloric acid, the solution is neutralised with sodium hydroxide and heated with an excess of sodium polysulphide. The insoluble sulphides are collected, washed, and dissolved in hot nitric acid, 10 c.c. of sulphuric acid are added, and the nitric acid expelled by heating. The residue is treated with water and the undissolved lead sulphate is dissolved in ammonium acetate and finally precipitated and weighed as chromate.

The filtrate from the lead sulphate is first neutralised and, after adding 2 c.c. of hydrochloric acid, treated with hydrogen sulphide to remove any remnant of tin and copper. The filtrate is boiled, mixed with 2 c.c. of bromine, the iron and manganese are jointly precipitated with ammonia, and finally separated in the usual manner. The filtrate is then treated with sodium sulphide and any zinc is collected as sulphide.

Arsenic, antimony, copper.—Ten grams of the sample are dissolved in 90 c.c. of nitro-hydrochloric acid, boiled to expel the nitric acid, rendered slightly alkaline with sodium hydroxide, and mixed with 50 grams of oxalic acid. The liquid is then diluted to 750 c.c., heated in the boiling water-bath, and treated for two hours with hydrogen sulphide. The precipitate is washed and digested with 10 c.c. of aqueous sodium hydroxide, which dissolves the arsenic and antimony and leaves any copper sulphide, which is then converted into oxide by calcination and finally estimated volumetrically or colorimetrically. The alkaline solution is acidified with hydrochloric acid in large excess and the arsenic collected and weighed as trisulphide, or it may be redissolved and finally weighed as magnesium ammonium arsenate. The acid liquid still retains antimony, which may be reprecipitated in the presence of oxalic acid by a current of hydrogen sulphide, as directed previously.

Sulphur.—Ten grams of the sample are dissolved in 100 c.c. of hydrochloric acid, and the gas evolved is passed through a series of absorption tubes containing zinc acetate solution. The zinc sulphide is then collected and titrated by means of standard iodine as usual. *Phosphorus.*—1.25 grams of the sample are dissolved in 30 c.c. of nitro-hydrochloric acid, and after evaporation the residue is dissolved in 10 c.c. of dilute hydrochloric acid (1:1) and treated in a 250 c.c. flask with hydrogen sulphide. The liquid is diluted to the mark, 200 c.c. of the

filtrate are boiled to expel the hydrogen sulphide, mixed with 10 c.c. of nitric acid, evaporated to 15 c.c., nearly neutralised with ammonia, and treated with excess of molybdate solution, and the yellow precipitate so obtained is finally weighed as such.

Tungsten, tin oxide.—Twenty-five grams of the metal are digested in the cold with a quantity of ferric chloride solution containing 50 grams of metallic iron and free from excess of acid. When the tin has dissolved, the insoluble matter is collected, washed with water slightly acidified with hydrochloric acid, and then ignited and weighed. It is then fused with 1 gram of sodium carbonate and 0.1 gram of nitre; the fused mass is dissolved in hydrochloric acid and evaporated to dryness, the residue is treated with 25 c.c. of dilute hydrochloric acid (1:1), and the undissolved matter dissolved in ammonia. The solution contains the tungsten which is recovered as tungstic acid by evaporating the solution and igniting the residue. The acid liquid contains the tin present in the sample as oxide and is treated with hydrogen sulphide as usual. A more correct estimation, however, of this tin is obtained by reducing the black deposit in a current of hydrogen at a red heat, and then dissolving the metal in hydrochloric acid.

Rapid estimation of tungsten and iron.—Ten grams of the sample are dissolved in 90 c.c. of nitro-hydrochloric acid, evaporated to a pasty consistency, redissolved in 40 c.c. of dilute hydrochloric acid (1:1), and diluted to 100 c.c. with boiling water. The insoluble matter, after being well washed with hot acidified water, is treated with ammonia, which dissolves the tungstic acid. On evaporating the solution and igniting the residue, pure tungsten trioxide is left.

Iron.—The acid liquid is rendered alkaline with sodium hydroxide, the iron precipitate is washed first with boiling water containing sodium hydroxide, then with plain boiling water. The precipitate is dissolved in hydrochloric acid, diluted to 200 c.c., and reduced by boiling with sodium hydrogen sulphite. After expelling the excess of sulphur dioxide, the heavy metals are precipitated with hydrogen sulphide, and after removing the excess of the latter by boiling, the iron is reoxidised with nitric acid, precipitated with ammonia, and finally weighed as oxide.

L. DE K.

Volumetric and Gravimetric Determination of Platinum.
ERWIN RUPP (*Arch. Pharm.*, 1904, 242, 143—156).—An approximately 4 per cent. potassium dichromate solution is made and standardised with *N*/20 thiosulphate solution. A 2.0—2.5 per cent. thallous nitrate solution is prepared and standardised against the dichromate as described in Abstr., 1903, ii, 183. Ten c.c. of the dichromate solution, about 1 gram of calcium carbonate, and 10 c.c. of the thallous nitrate solution are used, and of the filtrate 25 c.c. are mixed with 50 c.c. of water, 1—2 grams of potassium iodide, and 5 c.c. of 25 per cent. hydrochloric acid, and after 5 minutes are titrated with *N*/20 thiosulphate. For the estimation of platinum, the solution of platinic chloride is mixed with a considerable excess of the thallous nitrate solution in a 50 or 100 c.c. flask, allowed to remain in the cold for an hour with occasional gentle agitation, diluted to the mark, and filtered through a double filter from the precipitate of thallous

platinichloride; the excess of thallous salt is determined in an aliquot part of the filtrate as described above; 1 c.c. of $N/20$ thiosulphate = 0.0032465 gram of platinum. The platinum solution must contain but little free hydrochloric acid; otherwise some of the thallous salt will be precipitated as chloride. In five experiments, each with 0.046 gram of platinum, the error varied between -0.25 and $+0.5$ per cent. of the total amount.

For the gravimetric estimation, hydrazine hydrochloride is the most satisfactory reducing agent. The solution is diluted to about 100 c.c. in a conical flask; if any mineral acid is present, excess of sodium acetate is added; about 3 grams of hydrazine hydrochloride are added, and the whole is then heated on the water-bath until (after about two hours) the solution is quite clear. The precipitate is then collected on a double filter; this is dried and burned in a coil of platinum wire, and the residue is ignited in a crucible. In five experiments, each with 0.2 gram of platinum, the error varied between -0.3 and -0.05 per cent. of the whole.

In solutions of platinichloric acid (platinic chloride), the platinum can be estimated by evaporating to dryness in a glazed Rose crucible, heating the residue with a small flame, so that a gentle evolution of gas begins, continuing this heating in a fairly rapid current of hydrogen until (after about five minutes) no further smell of hydrogen chloride is noticeable, igniting, continuing the ignition after stopping the current of gas, and weighing. In four experiments, each with 0.2 gram of platinum, the error varied between 0.0 and $+0.4$ per cent. of the whole.

Ignited platinum in a more or less finely divided state should be weighed as soon as it is cold; in 24 hours, a gain in weight of 1 per cent. or more may occur. This is probably due to oxidation (Wöhler, this vol., ii, 44).

Peterson's iodometric method for the estimation of platinum (Abstr., 1899, ii, 253) is quite untrustworthy, even when modified as by Gooch and Morley in the case of gold (Abstr., 1900, ii, 110). C. F. B.

Hydroxylamine Salts in Qualitative Analysis. NAZARENO TARUGI (*Gazzetta*, 1903, 33, ii, 449—454).—Dilute aqueous solutions of platinic chloride are not reduced on adding a 20 per cent. solution of hydroxylamine hydrochloride mixed with an equal volume of ammonia; in more concentrated solutions, when the hydroxylamine is in excess, on warming, the compound $Pt(NH_2 \cdot OH)_4(OH)_2$ (Uhlenhuth, Abstr., 1900, ii, 485) is precipitated as a white, silky mass, insoluble in water; and when the platinic chloride is in excess, instead of this compound, Magnus's salt is produced, showing that reduction to platinous chloride must have taken place initially. These facts make impracticable the application of hydroxylamine to the separation of mercury, platinum, and gold in qualitative analysis, as suggested by Knoevenagel and Ebler (Abstr., 1902, ii, 697). Assuming that Uhlenhuth's base is, on reduction, precipitated with metallic gold and mercury, on dissolving in nitric acid the platinum goes into solution with the mercury, and the same objections apply as were brought forward in the case of hydrazine

salts (this vol., ii, 131). If Magnus's salt is formed, its insolubility in nitric acid and in aqua regia still more complicates the separation.

W. A. D.

Estimation of Thiocyanates in the presence of Chlorides, &c. A. DUBOSC (*Ann. Chim. anal.*, 1904, 9, 45—46).—The estimation of thiocyanates by means of silver nitrate is not applicable in the presence of chlorides or other compounds which precipitate silver solutions. The conversion of the sulphur into sulphate by means of potassium permanganate in acid solution gives indifferent results.

The sulphur contained in the thiocyanate may, however, be quantitatively converted into sulphate by mixing the solution with 2 grams of barium chloride, dissolved in 50 c.c. of water, and then adding 50 c.c. of an oxidising solution obtained by electrolysing brine and cooling the anode. This liquid contains some 20 grams of available chlorine per litre. After 10 minutes, 10 c.c. of hydrochloric acid are added, and the liquid is boiled. The barium sulphate so obtained is collected as usual.

Sulphates should be allowed for. Sulphides should be first removed by means of a suitable metallic salt.

L. DE K.

Jacquemin's Phenol Reaction; Detection of Oil of Cloves in Oil of Cinnamon. J. F. A. POOL (*Chem. Centr.*, 1904, i, 404; from *Pharm. Weekbl.*, 40, 1101—1103).—Jacquemin's reagent gives a blue coloration with those aromatic compounds which contain hydroxyl groups, and is, therefore, a valuable test for the detection of oil of cloves in oil of cinnamon, which does not contain such compounds. One c.c. of a dilute solution of aniline is mixed with a solution of sodium hypochlorite until the liquid assumes a violet colour, and a drop of the suspected oil is then added. If the oil of cinnamon is pure, a dirty violet liquid is obtained on shaking, which, after being diluted with water, yields a clear, violet filtrate, but if oil of cloves is present a green filtrate is obtained.

L. DE K.

Estimation of Starch by Hydrolysis with Hydrochloric Acid. ADELBERT RÖSSING (*Zeit. öffentl. Chem.*, 1904, 10, 61—64).—Two methods were tried. In the first (Sachsse's method), 3 grams of starch were boiled with 200 c.c. of water and 15 c.c. of hydrochloric acid of sp. gr. 1.125 for $2\frac{1}{2}$ hours in a reflux apparatus. After cooling, the solution was neutralised and diluted to 500 c.c. The dextrose was then estimated in 25 c.c. by Allihn's method. According to the second method, 2 grams of starch were boiled with 100 c.c. of water and 15 c.c. of hydrochloric acid of sp. gr. 1.19 for 2 hours in a reflux apparatus. The cold solution was then neutralised, diluted to 250 c.c., and filtered, if necessary. The dextrose was estimated as in the first method. Using the factor 0.9 to convert the dextrose into starch, too low results were obtained, but by employing the factor 0.94 for the first method, and 0.93 in the second, the quantity of starch found agreed with that actually present. The starches examined were wheat, potato, rice, maize, and arrowroot. Although trustworthy results were obtained

with pure starches, the hydrolysis method is unsuitable for estimating starch and dextrin in baked materials. W. P. S.

Detection of Salicylic Acid in Wines by a New Reaction. Behaviour of Wines in the Etna District with this Test. II. MATTEOSPICA (*Gazzetta*, 1903, 33, ii, 482—487. Compare Abstr., 1895, ii, 426).—Wines from the Etna district, which were known not to contain salicylic acid, responded to the test for this substance which has been already described (*loc. cit.*). It is shown that these wines contain a colouring matter which is responsible for the result. The test is, however, a perfectly trustworthy one if carbon disulphide is used instead of ethyl acetate in extracting the salicylic acid; in this solvent, the enolic acid which produces the confusion is insoluble. Or the dye produced upon the wool fibre may be dissolved off by an alkaline solution, and an attempt made to redeposit it upon a new fibre by the addition of acid; only when the yellow colour is transferable in this way to a second fibre can the presence of salicylic acid be inferred.

W. A. D.

Distinction between Boiled and Unboiled Milk. E. I. VAN ITALLIE (*Chem. Centr.*, 1904, i, 403; from *Pharm. Weekbl.*, 40, 1103—1104).—Boiled milk may be readily distinguished from unboiled milk by means of *p*-phenylenediamine and hydrogen peroxide, which give a blue colour with the unboiled samples. As the ferment which causes the coloration is not destroyed below 80°, pasteurised milk also gives a blue colour reaction. L. DE K.

Method of Estimating Formaldehyde prescribed by the German Pharmacopœia. CARL KIPPENBERGER (*Zeit. anal. Chem.*, 1903, 42, 686—696).—The method depends on the conversion of the formaldehyde into hexamethylenetetramine by treatment with a known excess of ammonia solution, and the estimation of the unconsumed ammonia by adding *N*-hydrochloric acid and titrating back with *N*-potassium hydroxide, using rosolic acid as indicator. The method is liable to several sources of error. The ammonia must be absolutely free from carbonate, otherwise it can only be accurately titrated with methyl-orange. A small but uncertain amount of the standard acid employed is consumed by combination with the hexamethylenetetramine, and at the same time part of the amine is decomposed both by the action of the acid and to a smaller extent by that of the alkali. A much more satisfactory method of estimation is found in the conversion of the formaldehyde into thioformaldehyde by the action of hydrogen sulphide. The formaldehyde solution is diluted to 10 volumes with water, then twice the volume of concentrated hydrochloric acid and some alcohol are added, and the hydrogen sulphide is passed through the liquid in a flask, connected with a second flask, to arrest any formaldehyde which may be expelled. After 24 hours, the precipitate is collected, freed from sulphur by washing with potassium sulphide, and then with water and alcohol, and finally dried and weighed. Concordant results are obtained, which do not agree with those yielded by the official method.

M. J. S.

Reaction of Aromatic and Fatty Aldehydes. SAMUEL S. SADTLER (*Amer. J. Pharm.*, 1904, 76, 84—87).—The following method is recommended for the estimation of citral in oil of lemon. A quantity of the oil, weighing 5 or 10 grams, is placed in a flask and neutralised with $N/2$ potassium hydroxide, rosolic acid being used as an indicator. Twenty-five or 50 c.c. of hot sodium sulphite solution (20 per cent.) are neutralised with $N/2$ hydrochloric acid, and afterwards added to the flask containing the oil. A red coloration is immediately produced and is discharged by the addition of $N/2$ hydrochloric acid. The flask is then heated and frequently shaken. Hydrochloric acid is added until the liquid no longer assumes a red colour, the quantity of acid used is noted, and the amount of citral is calculated, two mols. of hydrogen chloride being required for each mol. of citral.

The reaction is also applicable to the estimation of vanillin and fatty aldehydes. It may be employed for the detection and estimation of formaldehyde in milk, of acetone in wood spirit, and of acetaldehyde in grain spirit, and is especially suitable for the estimation of aldehydes in essential oils, such as those of cinnamon, cassia, bitter almonds, and lemon-grass. E. G.

Distinction between Chloral and Butylchloral. EMILIO GABUTTI (*Chem. Centr.*, 1904, i, 480—481; from *Boll. Chim. Farm.*, 42, 777—778).—An admixture of chloral with the more expensive butylchloral may be detected as follows: a solution of pyrogallol in pure 60 per cent. sulphuric acid, when gently heated with pure chloral, gives a blue solution, but with butylchloral the colour turns wine-red; in the case of a mixture, a more or less violet colour will appear. The blue colour caused by chloral changes, on addition of water, to a yellowish-brown, whilst the wine-red colour of butylchloral turns more or less violet. On addition of alkalis or ammonia, a clear yellow colour makes its appearance (also compare Abstr., 1901, ii, 11, 362),

L. DE K.

Detection of Acetone in Urine. ALEXANDRE C. VOURNASOS (*Bull. Soc. chim.*, 1904, [iii], 31, 137—139).—The author states that acetone may readily be detected in urine by the method already recommended by him for the detection of lactic acid in gastric juice (Abstr., 1902, ii, 364). In place of a solution containing iodine and methylamine, a solution of iodine (5 parts) in aniline (50 parts) may be employed. It is pointed out that alcohol, chloroform, and various acids, all of which may occur in urine, also give this reaction. Acetone may, however, be detected in presence of the acids by rendering the urine alkaline and distilling. T. A. H.

Nascent Sodium Hypobromite does not liberate all the Nitrogen of Urea. LEON GARNIER (*J. Pharm. Chim.*, 1904, [vi], 19, 137—139. Compare Abstr., 1900, ii, 699).—Although the disengagement of nitrogen is complete when 2 c.c. of 1 per cent. urea solution are treated by the method of Le Comte (Abstr., 1903, ii,

518), the method fails to give complete evolution with solutions of 2 per cent. strength. Admixture of dextrose raises the amount of nitrogen evolved.

G. D. L.

Two New Reactions of Acetanilide. ETIENNE BARRAL (*J. Pharm. Chim.*, 1904, [vi], 19, 237).—Phosphomolybdic acid gives, with a solution of acetanilide, a bright yellow precipitate, soluble on warming, which distinguishes it from the yellow precipitate given by phenacetin, which is insoluble on warming.

Mandelin's reagent with acetanilide gives a red colour rapidly changing to greenish-brown, whilst with phenacetin the coloration is olive-green in the cold, becoming reddish-brown on warming.

G. D. L.

Isolation of the Alkaloids in Chemico-legal Cases. CARL KIPPENBERGER and L. VON JAKUBOWSKI (*Zeit. anal. Chem.*, 1903, 42, 696—707).—A comparison of Kippenberger's glycerotannic method (Abstr., 1895, ii, 465; 1901, ii, 79) with those of Stas-Otto, Hilger-Küster, and Dragendorff, when applied to the human stomach, intestines, spleen, and liver, free from vegetable alkaloids, gave the general result that the last three methods all yielded final solutions containing impurities which gave alkaloid reactions with iodine solution, phosphomolybdic acid, picric acid, and mercuric chloride, whilst the final solution obtained by the first-named method was markedly freer from impurities, and gave no precipitates with the above reagents.

M. J. S.

Amount of Caffeine in the Coffee used as a Beverage. JULIUS KATZ (*Arch. Pharm.*, 1904, 242, 42—48).—A satisfactory method for the estimation of caffeine has been devised (*Ber. deut. pharm. Ges.*, 1902, 12, 250). As applied to the analysis of roasted and ground coffee it is as follows: of the powder, 10.0 grams are shaken mechanically with 200.0 c.c. of chloroform and 10.0 c.c. of "ammonia" for half an hour. After the solid has settled, 150.0 c.c. of the chloroform is filtered off through a Sanders "cigarette-filter," the chloroform distilled off, the residue mixed with 10 c.c. of 0.5 per cent. hydrochloric acid, and a few c.c. of ether, the ether boiled off on the water-bath after the addition of about 0.5 gram of solid paraffin, and the residue heated till the paraffin has melted completely. After the liquid has cooled, it is filtered through a wet filter, and the residue warmed twice in succession with 10 c.c. of 0.5 per cent. hydrochloric acid and filtered; the united filtrate is extracted with chloroform for 2 hours in a Katz percolator, the chloroform evaporated, and the residue of crude caffeine weighed. The crude caffeine is then dissolved in 10 c.c. of water (with the addition of a few drops of ether, which are then boiled off); the hot solution is heated for 10 minutes with 3 c.c. of a suspension of lead hydroxide in water (1:20), mixed with about 0.2 of calcined magnesia, and filtered, the residue being washed with water; the filtrate is extracted with chloroform for 2 hours in the percolator, the chloroform evaporated, and the residue of pure caffeine weighed.

The sample of coffee examined contained 1.34 per cent. of crude,

1.26 of pure caffeine. In the preparation of the beverage, 300 c.c. of boiling water were used with 15.0 grams of the ground coffee. When a special coffee apparatus (Arndt's) was used, the liquid contained 96.5 per cent. of the caffeine in the powder used. When the boiling water was poured over the ground coffee and the mixture boiled for 5 minutes, according to the prescription of the German pharmacopœia, 85 per cent. was present. When the boiling water was simply poured over the coffee resting on filter-paper in an ordinary coffee funnel or sieve, only 60 per cent. of the total caffeine was obtained in the liquid. Prepared by either of the first two methods, a cup of coffee holding 150 c.c. contains about 0.1 gram of caffeine. The amount of total solid matter extracted runs roughly parallel to the amount of caffeine, varying from 0.8 to 1.5 per cent. of the liquid according to the method employed.

The result was much the same whether distilled water was used or the Leipzig town supply with 8.75 degrees of permanent and 4.0 of total hardness (parts CaCO_3 per 100,000 of water). The addition of 0.1 per cent. of sodium hydrogen carbonate to the latter had but little effect.

C. F. B.

Colour Reactions of Pilocarpine. ETIENNE BARRAL (*J. Pharm. Chim.*, 1904, [vi], 19, 188—189).—When boiled with sodium persulphate, a dilute solution of pilocarpine gives foetid, faintly ammoniacal vapours, which blue turmeric and blacken mercurous nitrate. Several drops of the pilocarpine solution warmed with sulphuric acid and formaldehyde give a yellow colour, changing to brownish-yellow, blood-red, and finally brownish-red.

Mandelin's reagent gives, on warming, a golden-yellow, changing to a clear green, and finally to a blue colour, which is unaltered by dilution.

A 1 per cent. solution of potassium permanganate in concentrated sulphuric acid on warming is at first decolorised, then becomes yellow, and gives vapours smelling like burnt tartaric acid.

G. D. L.

A Ptomaine Resembling Veratrine. STÜBER (*Zeit. Nahr. Genussm.*, 1903, 6, 1137—1138).—During an investigation as to the cause of the death of over 100 rats, the bodies of which were found in the hold of a ship, it was found that, whilst no metallic poisons or plague bacteria were present, a substance could be obtained from the bodies, by the usual methods for separating the alkaloids, which closely resembled veratrine in some of its chemical reactions. The purified substance consisted of a yellow, amorphous mass. When a trace of the latter was warmed with concentrated sulphuric acid, a brilliant cherry-red solution was obtained, exactly similar to that given by pure veratrine. The ptomaine gave precipitates with iodine and tannin solutions, but did not react with platinic or mercuric chlorides. It differed from veratrine in producing no muscular contractions when injected into a frog.

W. P. S.

Estimation of Quinotannates in de Vrij's Cinchona Extract. JULES WARIN (*J. Pharm. Chim.*, 1904, [vi], 19, 233—236).—The precipitation and weighing of alkaloid quinotannates from this extract by the addition of sodium acetate does not give correct quantitative results, since about one-fifth of the alkaloids remain unprecipitated, whilst a further smaller proportion is taken up by the washing water.

For comparative purposes it is therefore necessary to operate under similar conditions, and it is preferable to determine quinotannate after extraction of the alkaloids from ammoniacal solution. G. D. L.

Estimation of Indoxyl by Nitration of the Indigo Dyes. LOUIS MAILLARD (*Compt. rend. Soc. Biol.*, 1903, 55, 1506—1508).—Whilst admitting that Monfet's method, which consists in nitration of the indigo dyes (indigotin, indirubin), and then estimating colorimetrically the picric acid formed, can, if carried out properly, be considered exact, the author still holds that the method of sulphonation has the advantage. W. D. H.

Estimation of Indican in Urine. ALEXANDER ELLINGER (*Zeit. physiol. Chem.*, 1904, 41, 20—32).—Polemical against Bouma and Maillard. W. D. H.

Sensitive Test for Bile Pigments in Urine. ADOLF JOLLES (*Zeit. anal. Chem.*, 1903, 42, 713—716).—About 10 c.c. of the urine are shaken up with 1 c.c. of chloroform and 4—5 c.c. of a 10 per cent. barium chloride solution and left in repose for a minute. The supernatant liquid is removed and the residue treated with 2—3 c.c. of an *N*/100 Hübl iodine solution and 1 c.c. of concentrated hydrochloric acid, shaken, and allowed to settle. If bile pigments are present, the precipitate, the chloroform, and the aqueous layer are all coloured green to greenish-blue. About 0.1 mg. of bilirubin in 100 c.c. of urine is the lower limit of the reaction. With highly concentrated urines, especially those rich in indican, a more complete removal of the urine from the chloroform is necessary. It is recommended to use 2—3 c.c. of chloroform and 1 c.c. of barium chloride and to use a centrifuge, washing subsequently 2 or 3 times with water. The precipitate is then shaken with 5 c.c. of alcohol and 2—3 drops of the following iodine solution: 0.63 gram of iodine and 0.75 gram of mercuric chloride are each dissolved in 125 c.c. of alcohol; the solutions are mixed, and 250 c.c. of concentrated hydrochloric acid are added. This solution can be preserved for a long time in brown glass bottles. M. J. S.

Estimation of Bilirubin in Serum. A. GILBERT. M. HERSCHER, and SWIGEL POSTERNAK (*Compt. rend. Soc. Biol.*, 1903, 55, 1587—1590).—The method devised is a colorimetric one, namely, the intensity of the Gmelin reaction. It is, however, based on the assumption that the normal pigment of blood serum is bilirubin. W. D. H.

Estimation of Albumin in Serums. EMIL REISS (*Chem. Centr.*, 1904, i, 481—482; from *Arch. exp. Pathol. Pharm.*, 51,

18—29).—The index of refraction of the serum is taken, and after allowing 0.00277 for non-albuminous matters and 1.3320 for the refraction of pure water, the remainder is divided by 0.00172; the result represents the percentage of albumin. L. DE K.

Estimation of an Organic Phosphorus Compound in Grape Stones and Wines. T. WEIRICH and G. ORTLIEB (*Chem. Zeit.*, 1904, 28, 153—154).—Wine contains a lecithin which may be extracted from the residue by means of absolute alcohol. Phosphorus is then estimated in the usual way, and from this the amount of real lecithin in the extract is calculated. This lecithin is, however, rapidly decomposed at an elevated temperature. In conducting the experiments, the sample should be evaporated in vacuum, or at all events at a temperature not exceeding 50°. It is also sensibly soluble in ether or chloroform. L. DE K.

Macroscopic Detection of Leucocytosis. CARL HIRSCH and ED. STADLER (*Zeit. physiol. Chem.*, 1904, 41, 125—127).—The well-known method of detecting pus in urine by the gelatinous mass produced by adding strong alkali is due to the formation of sodium nucleate. The same reaction may be successfully employed as a naked eye test for excess of leucocytes in blood. W. D. H.

The Reactions for the Oxidising Enzymes of Cow's and Human Milk. W. RULLMANN (*Zeit. Nahr. Genussm.*, 1904, 7, 81—89).—By heating cow's milk for 1 hour at a temperature of 68—69°, practically all bacteria were destroyed, but the enzymes were not affected unless the temperature exceeds 70°. A number of experiments are given, in which the usual tests for detecting oxydase were employed, the results showing that the enzyme is present in milk sterilised at a temperature not exceeding 70°. The *p*-phenylenediamine hydrochloride test was found to be the most sensitive for this purpose.

Oxydase was detected in human milk by the above-mentioned test 40 days after parturition. The guaiacum test gave negative results after the 28th day. W. P. S.

General and Physical Chemistry.

Satellite Rays in the Cadmium Spectrum. CHARLES FABRY (*Compt. rend.*, 1904, 138, 854—856).—When the ray 508·6 of the cadmium spectrum is examined by means of the interference spectro-scope (compare Fabry and Perot, *Ann. Chim. Phys.*, 1899, [vii], 16), it is found to consist of two rays of unequal intensity, or of three rays of equal intensity, according as the metallic vapour is illuminated in a tube with aluminium electrodes or without electrodes (compare Hamy, *Compt. rend.*, 1900, 130, 700). In the latter case, as observed by Hamy, the presence of a small quantity of air in the tube causes two of the rays to become very feeble, whilst in the former case the substitution of electrodes of fused cadmium for those of aluminium causes the ray 508·6 to present the triple appearance it exhibits in the tube without electrodes. It appears, therefore, that absolute purity of the luminous gas is a necessary condition for the satisfactory appearance of satellite rays, a condition which Bouty also found to obtain in the case of argon (compare this vol., ii, 309). M. A. W.

Ultra-violet Spectra of a Tautomeric Compound. R. MAGINI (*Atti R. Accad. Lincei*, 1904, [v], 13, i, 104—108. Compare Abstr., 1903, ii, 706, and this vol., ii, 107).—The author has examined the ultra-violet absorption spectra of two samples of ethyl acetoacetate, one of which was stated by Schiff to be the pure enolic modification, and the other to consist of about equal proportions of the enolic and keto-forms. The differences between the two spectra are very slight, as also are those produced by distilling the liquids, and do not admit of any conclusion being drawn as to the existence of keto- and enolic modifications of ethyl acetoacetate. T. H. P.

Action of Chemical and Osmotic Phenomena on Phosphorescence. M. LAMBERT (*Compt. rend.*, 1904, 138, 626—627).—The production of *N*-rays by the opening of a previously closed Leclanché cell (compare Jégou, *Compt. rend.*, 1904, 138, 491) is to be attributed to the chemical action taking place in the cell when the circuit is closed, which, owing to polarisation, persists when the circuit is open. In the case of a dichromate cell, in which the chemical action proceeds in open circuit and the phenomenon of polarisation is very marked, the production of *n*-rays, as detected by the increased brightness of a phosphorescent screen, is apparent even without closing the circuit.

The osmotic phenomenon occurring in voltaic elements containing two liquids separated by a porous septum forms another probable source of *n*-rays, for the author finds that a phosphorescent screen becomes brighter when it is placed near a vessel containing a 0·7 per cent. solution of sodium chloride separated by parchment from a more concentrated solution of the same salt. M. A. W.

Emanation given off by Radium. J. A. McCLELLAND (*Phil. Mag.*, 1904, [vi], 7, 355—362).—The object of the experiments was to test as accurately as possible whether the emanation from radium carries with it an electric charge, and a description of the apparatus and method of working is given. The results indicate that the emanation is not charged. The radium atom gives off positively charged particles—the α -rays. The emanation cannot be what remains of the atom after the emission of these rays, as it would then be negatively charged; the atom must have therefore parted with an equal negative charge either by the emission of negative particles, or in some other way. L. M. J.

Radioactivity of Certain Minerals and Mineral Waters. ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1904, 73, 191—197).—A number of minerals are known to be radioactive, and the experiments were made with the object of ascertaining whether any unknown radioactive matter is indicated in these minerals. The method adopted was to heat the crude mineral and examine the rate of decay of the emanation given off. Although small quantities of an emanation less durable than that of radium might escape detection, any emanation more durable would have been recognised. The minerals examined were samarskite from N. Carolina, fergusonite from Norway (?), pitchblende from Cornwall, malacone from Norway, monazite from Norway, N. Carolina, and Brazil, and zircon from N. Carolina. No new emanation was recognised, the results in all cases indicated radium. Malacone contains argon as well as helium, but no new radioactive element was indicated. The only mineral yielding thorium emanation was monazite from Norway. A small quantity of red deposit from the water of the King's Spring at Bath was examined. It was found to be active, the activity being due to radium, and the same result was found for other Bath spring deposits, whilst radium was also found in the water. The author calculates the annual delivery of radium by the spring to be about one-third gram, and of helium about 1000 litres. This ratio is of the same order as in the radioactive minerals. L. M. J.

Law of Disappearance of Induced Radioactivity after Heating the Active Substance. PIERRE CURIE and J. DANNE (*Compt. rend.*, 1904, 138, 748—751. Compare Abstr., 1903, ii, 50, 255).—The effect of heating a substance which has been rendered radioactive by induction is to distil the radioactivity on to neighbouring substances (compare Gates, *Phys. Review*, May, 1903). An examination of the disappearance of induced radioactivity from plates which have been heated at various temperatures shows that the rate of decrease of activity tends towards the simple exponential expression $I = I_0 e^{-c't}$, c' varying with the temperature of heating, first increasing with the temperature up to 1100°, then diminishing.

In another series of experiments, the induced radioactivity of a platinum wire was distilled on to a surrounding platinum cylinder, which was then examined in respect of the rate of disappearance of the activity, with the result that the activity first increases, reaches a maximum, and then falls off. If, however, the distillation is effected

in two fractions, the rate of decrease of the induced radioactivity due to the second distillation at the higher temperature can be expressed by a simple exponential expression.

These facts can be explained on the hypothesis that below 600° the substance B only distils, leaving the original plate radioactive with C , the rate of decrease of which is given by a simple exponential expression; at higher temperatures, 700° , C also distils, whilst at still higher temperatures the nature of C is modified. In the case of the plates on to which the induced radioactivity has been distilled, below 600° B only is condensed and slowly changes into C , at higher temperatures both B and C condense. M. A. W.

Action of Canal Rays on Aluminium and Zinc Oxides. GERHARD C. SCHMIDT (*Ann. Physik*, 1904, [iv], 13, 622—633. Compare Abstr., 1903, ii, 50).—In a previous paper (*loc. cit.*), the author adopted the view that zinc oxide generally fluoresces under the action of canal rays, because it contains an admixture of foreign oxide in solid solution. This view was adversely criticised by Tafel (*Ann. Physik*, 1903, [iv], 11, 613), who regarded the fluorescence as the sequel of a transformation into another modification. In the present paper, the author records further experiments, showing that aluminium and zinc oxides do not fluoresce when absolutely pure, but only when they contain an admixture of other oxide (for example, of chromium and cadmium respectively) in solid solution. J. C. P.

The Possibility of Showing by a Contrast Phenomenon the Objective Action of n -rays on Luminous Calcium Sulphide. J. MACÉ DE LÉPINAY (*Compt. rend.*, 1904, 138, 798—799).—Taking advantage of the fact discovered by Blondlot (*Compt. rend.*, 1904, 138, 547) that the action of the n -rays on luminous calcium sulphide is reversed when the surface of the latter is viewed in a very oblique direction, the author describes a device by means of which the objective effect of n -rays can be appreciated by observers who are unable to discern the ordinary action of the rays. The arrangement consists of two luminous calcium sulphide screens, one large one (20 cm. \times 2 cm.), placed in a horizontal plane with its long axis parallel to the direction of vision, and one small one (2 cm. \times 0.2 cm.), placed in a vertical plane normal to the direction of vision and so inclined that, when the large screen is viewed in such an oblique direction that it looks like a narrow line, the appearance of the combination is that of the figure 7, the oblique branch of which is seen under normal, and the other under oblique incidence. When n -rays act simultaneously on the two luminous surfaces, the oblique branch of the 7 becomes brighter, whilst the other either becomes darker, or disappears altogether. M. A. W.

Standard Electrodes. LUDWIG SAUER (*Zeit. physikal. Chem.*, 1904, 47, 146—184).—The author has made a detailed study of the following electrodes: (a) $\text{Hg} \mid \text{HgCl}, 1.0N\text{KCl}$;

(b) $\text{Hg} \mid \text{HgCl}, 0.1N\text{KCl}$; (c) $\text{Hg} \mid \text{HgCl}, 1.0N\text{HCl}$;

(d) $\text{Hg} \mid \text{HgCl}, 0.1N\text{HCl}$; (e) $\text{Hg} \mid \text{Hg}_2\text{SO}_4, 1.0N\text{H}_2\text{SO}_4$;

(f) $\text{Hg} \mid \text{Hg}_2\text{SO}_4, 0.1N\text{H}_2\text{SO}_4$.

With due care in their preparation, it is possible to reproduce the *E.M.F.* of these electrodes within the following limits: (*a*), (*c*), (*e*), and (*f*) 0.1 millivolt; (*b*) 0.2 millivolt; (*d*) about 2 millivolts. The method adopted in preparing the electrode is to make a paste of the mercury and the depolariser by shaking them for a short time. In this way, a constant *E.M.F.* is obtained from the beginning. Assuming that the *E.M.F.* of (*a*) at 18° is 0.560 volt, the values obtained for the others at 18° are as follows: (*b*) +0.612 volt; (*c*) +0.554 volt; (*d*) +0.611 volt; (*e*) +0.962 volt. Incidentally, it was found that calomel is more soluble when finely divided than in the form of larger crystals (compare Ostwald, *Abstr.*, 1900, ii, 712).

J. C. P.

Polarisation of Platinum, Gold, and Palladium Electrodes. E. ROTHÉ (*Ann. Chim. Phys.*, 1904, [viii], 1, 289—237).—The *E.M.F.* of polarisation of platinum electrodes in acidified water varies continuously as the external *E.M.F.* increases. The curve obtained by plotting the *E.M.F.* as abscissæ and the deviations as ordinates shows an angular point in the neighbourhood of 1.55 volts, at which value the decomposition of the water begins.

The polarisation is to be attributed to the modification of the electrodes by their absorption of the ions with the formation of definite chemical compounds, hydrides, or oxides. In the case of two electrodes of unequal sizes, the smaller becomes modified before the larger, and therefore visible electrolysis may occur temporarily at that electrode when the external *E.M.F.* is much lower (1 volt) than the minimum value.

Similar results were obtained with gold and palladium electrodes.

M. A. W.

Dielectric Constants of some Inorganic Solvents. HERMAN SCHLUNDT (*J. Physical Chem.*, 1904, 8, 122—130).—An extension of the author's previous work (*Abstr.*, 1902, ii, 2). The results obtained are as follows:

| Substance. | <i>D. C.</i> | <i>T.</i> | Substance. | <i>D. C.</i> | <i>T.</i> |
|-----------------------------|--------------|-----------|---------------------------|--------------|-----------|
| Phosphorus trichloride ... | 3.72 | 18° | Antimony tribromide ... | 20.9 | 100° |
| Phosphorus tribromide | 3.88 | 20 | „ „ (solid) | 5.05 | 20 |
| Phosphorus tri-iodide | 4.12 | 65 | Antimony tri-iodide ... | 13.9 | 175 |
| „ „ (solid) | 3.66 | 20 | „ „ (solid) | 9.1 | 20 |
| Arsenic trichloride | 12.6 | 17 | Phosphorus | 3.85 | 45 |
| „ „ (solid) | 3.6 | — 50 | „ „ (liquid) | 3.85 | 20 |
| Arsenic tribromide | 8.83 | 35 | „ „ (solid) | 4.1 | 20 |
| „ „ (solid) | 3.33 | 20 | Silicon tetrachloride ... | 2.40 | 16 |
| Arsenic tri-iodide | 7.0 | 150 | Nitrogen peroxide | 2.56 | 15 |
| „ „ (solid) | 5.38 | 18 | „ „ (solid) | 2.6 | — 40 |

In most cases, the dielectric constant is considerably less in the solid than in the liquid state, the change occurring during solidification. Of the substances observed, phosphorus trichloride, phosphorus tribromide, and silicon tetrachloride do not possess ionising power; they have low dielectric constants, and hence follow the Nernst-Thompson rule. Antimony trichloride has good, and arsenic trichloride fair, ionising power, this again being in accord with the rule (compare

Walden, Abstr., 1901, ii, 11). Nitrogen tetroxide was found by Frankland to have no ionising power (Trans., 1901, 79, 1356), its constant is also low.
L. M. J.

Dielectric Cohesion of Argon and its Mixtures. E. BOUTY (*Compt. rend.*, 1904, 138, 616—618).—The dielectric cohesion of argon is 6·8 times more feeble than that of hydrogen and 14 times more feeble than that of air, and for a constant volume the value is independent of the temperature. The addition of traces of foreign gases causes such a marked increase in the dielectric cohesion of argon that it forms almost as sensitive a test of the purity of the gas as that afforded by the spectrum.
M. A. W.

Theory of Amphoteric Electrolytes. JAMES WALKER (*Proc. Roy. Soc.*, 1904, 73, 155—165).—Many substances are capable of behaving either as acids or as bases, and these have been termed amphoteric electrolytes. Although the dissociation constants, both with respect to their ionisation as acids and bases, have been determined for many such compounds by Winkelblech (Abstr., 1901, ii, 370), yet the theory has not been completely worked out and is now developed by the author on the basis of the mass-action law, and the electrolytic dissociation theory of Arrhenius. The various equations are deduced by means of which the concentration of the various ions may be determined if the concentration of the unionised compound, and the dissociation constants for the substance as acid and as base are known. It is pointed out that the conductivity is in such cases no measure of the ionisation. The effect of even feebly marked basic character is well exemplified by the comparison of the concentration of the positive ions in a simple acid, where $k_a = 10^{-5}$, and in amphoteric electrolytes with similar acid dissociation, but a basic dissociation of from 1.2×10^{-14} to 1.2×10^{-11} . Ostwald obtained for *o*-aminobenzoic acid values for the dissociation constant which steadily increased with dilution and suggested that this was due to the existence of double molecules (Abstr., 1889, 818). The assumption is, however, unnecessary as the facts are in accord with the author's theoretical conclusions. It is further shown that the values obtained by Ostwald and Winkelblech for the three aminobenzoic acids are in good quantitative agreement with the values calculated on the basis of the theoretical deductions.
L. M. J.

Electrical Reduction. FRITZ HABER and RUDOLPH RUSS (*Zeit. physikal. Chem.*, 1904, 47, 257—335. Compare Haber, Abstr., 1900, i, 281, 282, 592; ii, 257; Russ, Abstr., 1903, ii, 631).—The electrical reduction of nitrobenzene and *p*-nitrophenol in alkaline solution is governed by the expression $E = xRT/2 \cdot \log I/C - A$, where E is the fall of potential at the cathode, I the current strength, and C the concentration of the depolariser, A is a constant, and x , whilst theoretically equal to unity, is found to be greater. The geometrical interpretation of the value of x previously advanced by Haber is not confirmed, and x apparently varies with the nature of the electrode.

The authors have studied the equilibria involved in the following

reactions : (1) quinone + hydrogen iodide = iodine + quinol ; (2) quinone + hydrogen = quinol ; (3) iodine + hydrogen = hydrogen iodide. They find that reactions (1) and (2) proceed with a measurable velocity towards equilibrium, whilst (3) takes place with great rapidity. The quinone-quinol electrode was polarised, and its behaviour found to be in accordance with Haber's views. The phenomena observed, however, when the iodine (hydrogen iodide) electrode is polarised are quite different, and are to be referred not to velocity of reaction, but to velocity of diffusion.

J. C. P.

Influence of the Cathode Material on the Electrolytic Reduction of Nitrobenzene. WALTHER LÖB and ROY W. MOORE (*Zeit. physikal. Chem.*, 1904, 47, 418—444. Compare Löb, *Abstr.*, 1903, i, 20).—Nitrobenzene has been reduced in alkaline solution with a cathode of platinum, copper, tin, zinc, lead, or nickel, or with a platinum cathode + the hydroxide of tin, zinc, or lead. The cathode potential difference has been kept the same throughout, and under these conditions the same reduction products in approximately the same quantities are obtained whatever be the material of the electrode. In other words, it is the cathode potential that is the measure of the reducing energy. This is in agreement with Haber's views, but the authors reject the grounds on which these are based, and suggest a more adequate conception of the mechanism of reduction.

J. C. P.

General Relations between the Heat of Combustion of Organic Compounds and their Constitutional Formula. Calculation of the Heats of Combustion. PAUL LEMOULT (*Ann. Chim. Phys.*, 1904, [viii], 1, 496—553).—A *résumé* of work already published (compare *Abstr.*, 1903, ii, 410 ; this vol., ii, 12).

M. A. W.

Use of Acetylene Gas for Heating Germinating Stoves by means of an Automatic Temperature Regulator. H. JOFFRIN (*Compt. rend.*, 1903, 138, 817—819).—The temperature regulator described and depicted in the paper maintains the temperature between two limits by extinguishing the flame at the maximum and rekindling it at the minimum temperature. The arrangement consists essentially of a long alcohol thermometer communicating with a U-tube of mercury, the two fixed rigidly to a horizontal beam capable of oscillating about a knife edge in the centre, and carrying at one end a reservoir of mercury which feeds another U-tube through which the acetylene passes. The expansion and contraction of the alcohol raises or lowers the beam, and the gas supply is thereby cut off and the flame extinguished, or turned on and rekindled by a neighbouring permanent flame. There are mechanical arrangements by means of which the amplitude of the oscillation and therefore the range of temperature can be limited at will.

M. A. W.

Law of the Rectilinear Diameter. Relation between Heat of Vaporisation and the Critical Constants. GERRIT BAKKER (*Zeit. physikal. Chem.*, 1904, 47, 231—232. Compare *Zeit. physikal. Chem.*,

1895, 18, 646).—A criticism of Batschinski's treatment (Abstr., 1903, ii, 10) of the above topics. J. C. P.

Vapour Pressures in the System: Benzene, Carbon Tetrachloride, and Ethyl Alcohol. I. FRANS A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 1904, 47, 445—470).—The author has first studied the vapour pressures of the binary systems obtained by taking the three above-mentioned components in pairs. The vapour pressure curves for (1) alcohol and carbon tetrachloride, (2) alcohol and benzene, exhibit maxima. That for benzene and carbon tetrachloride has neither maximum nor minimum. The author has determined also the vapour pressures of a large number of the ternary mixtures, which are all homogeneous. The results may be represented by the usual graphical methods. J. C. P.

Vapour Tension of Liquid Mixtures (for example, of Bromine and Iodine) in Cases where a Partially Dissociated Compound is formed. JOHANNES J. VAN LAAR (*Zeit. physikal. Chem.*, 1904, 47, 129—145).—A theoretical paper, unsuitable for abstraction. J. C. P.

More Exact Equation of Condition for Gases. J. B. GOEBEL (*Zeit. physikal. Chem.*, 1904, 47, 471—489).—The author has arrived at the equation $p = RT/(v - b) - a/(v - a)^2$, in which p , v , R , and T have their usual significance. The quantity b is in general variable with the pressure, and $= b_0 - b_1 p$, but the values of a , α , b_0 , and b_1 vary only with the nature of the gas under consideration. Tested over a considerable range of temperatures and volumes, the formula gives values of p in satisfactory agreement with the experimental work of Amagat and others on carbon dioxide, ethylene, and nitrous oxide. The critical constants may also be calculated in close agreement with the experimentally determined values for the above gases as well as for nitrogen, oxygen, and air.

The following table shows the values of the constants for the various gases:

| | R . | a . | α . | b_0 . | b_1 |
|-------------------|----------|---------|------------|---------|---------------------|
| Carbon dioxide... | 0·003681 | 0·00734 | 0·00044 | 0·00238 | 0·0 |
| Ethylene ... | 0·003684 | 0·00917 | 0·00068 | 0·00329 | 0·0 |
| Nitrous oxide ... | 0·003682 | 0·00749 | 0·00044 | 0·00238 | 0·0 |
| Nitrogen ... | 0·003664 | 0·00281 | 0·00068 | 0·00250 | 0·0 ₅ 13 |
| Oxygen ... | 0·003666 | 0·00272 | 0·00060 | 0·00205 | 0·0 ₆ 9 |
| Air ... | 0·003665 | 0·00279 | 0·00065 | 0·00236 | 0·0 ₅ 11 |

The values of the critical constants involved in the respective equations are as follows:

| | t_k . | p_k . | v_k . |
|--------------------|---------|---------|---------|
| Carbon dioxide ... | 31° | 72 | 0·00626 |
| Ethylene ... | 10 | 50 | 0·00850 |
| Nitrous oxide ... | 36·4 | 73·1 | 0·00628 |
| Nitrogen ... | -145 | 33 | 0·00602 |
| Oxygen... | -117 | 50·8 | 0·00482 |
| Air ... | -138 | 37 | 0·00566 |

J. C. P.

Cryoscopic Researches on Solutions of Gases in Liquids. FELICE GARELLI and PIETRO FALCIOLA (*Atti R. Accad. Lincei*, 1904, [v], 13, i, 110—118).—The authors have determined the depressions of freezing point caused by dissolving varying proportions of gases in certain solvents. For a saturated solution of hydrogen sulphide in water, the depression is slightly greater than the normal value ($i=1.09$), so that at the freezing point of such a solution, hydrogen sulphide is dissociated to only a small extent; the dissociation increases moderately rapidly with the dilution. With solutions of carbon dioxide in water, containing from 0.25 to 0.35 gram of the gas per 100 grams of solvent, a constant and slight dissociation ($i=1.11$) is observed. In benzene, carbon dioxide and acetylene exhibit the normal molecular weights within fairly wide limits of concentration.

By the same method, the coefficients of absorption of hydrogen sulphide, carbon dioxide, acetylene, and nitrous oxide in various solvents have been measured, the grams of gas dissolved per 100 grams of solvent being given in the following table:

| | Temperature. | H ₂ S. | | CO ₂ . | | C ₂ H ₂ . | | N ₂ O. | |
|------------------|--------------|---------------------|----------------|---------------------|----------------|---------------------------------|----------------|---------------------|----------------|
| | | Maximum depression. | Concentration. | Maximum depression. | Concentration. | Maximum depression. | Concentration. | Maximum depression. | Concentration. |
| Water | 0.0° | 0.395° | 0.658 | 0.165° | 0.350 | 0.08° | 0.1118 | 0.105° | 0.2483 |
| Benzene | 5.5 | — | — | 0.770 | 0.664 | 1.440 | 0.734 | 0.725 | 0.6255 |
| Bromoform..... | 7.0 | — | — | 0.200 | 0.061 | 0.581 | 0.1050 | — | — |
| Acetophenone.. | 16.0 | 0.50 | 0.302 | 0.560 | 0.440 | 1.493 | 0.697 | 0.255 | 0.2003 |
| Acetic acid..... | 15.5 | — | — | 0.930 | 1.049 | 1.048 | 0.6984 | — | — |
| Formic acid ... | 7.5 | — | — | 0.530 | 0.904 | 0.402 | 0.3720 | — | — |

These values agree well with those found by direct measurement of the absorbed gases.

T. H. P.

Influence of Temperature and Pressure on the Absorption and Diffusion of Hydrogen in Palladium. G. N. ST. SCHMIDT (*Ann. Physik*, [iv], 13, 747—769).—It is found that the volume of hydrogen absorbed by palladium increases with fall of temperature to about 140°; below this, concordant results are not obtained. The absorption curve between about 140° and 300° is approximately a straight line, but the accuracy of the experiments is not such as to show if the curve is rigorously linear. The absorption is found to increase with pressure. The diffusion, however, increases with temperature as well as with pressure. Numerous tables of results are given, the temperatures varying from about 150° to 300°, and the pressure from 100 mm. to 300 mm. The author considers that the temperature curve is probably quadratic, but no numbers are given in verification. The pressure curve for the higher pressures is probably linear.

He does not consider Winkelmann's assumption of the dissociation of the hydrogen molecules to be necessary (Abstr., 1902, ii, 552). L. M. J.

Compressibilities of Oxygen, Hydrogen, Nitrogen, and Carbon Monoxide between One Atmosphere and Half an Atmosphere of Pressure, and on the Atomic Weights of the Elements concerned. LORD RAYLEIGH (*Proc. Roy. Soc.*, 1904, 73, 153—154).—A complete account of the method is deferred; the results obtained for the quotients of the values of pv at the half atmosphere by the corresponding values at the whole atmosphere were: oxygen, 1·00040; hydrogen, 0·99976; nitrogen, 1·00017; carbon monoxide, 1·00028. The ratio of the densities at great rarefaction is calculable from these, and it is found the correction factors are, hydrogen, 1·00128; nitrogen, 1·00046; carbon monoxide, 1·00024; oxygen being taken as the standard. It follows that at atmospheric pressure the volume of hydrogen which combines with one volume of oxygen should be 2·0026 volumes, a number in good accord with the value 2·00245 found by Scott, and 2·0027 found by Morley. The densities at atmospheric and very small pressures respectively, referred to oxygen = 16, are: hydrogen, 1·0075, 1·0088; nitrogen, 14·003, 14·009; carbon monoxide, 14·000, 14·003. The value 14·05 obtained by Stas for nitrogen hence appears impossible if Avogadro's law be strictly true. L. M. J.

Diminution of the Density of Certain Substances Induced by Compression and the Cause of this Phenomenon. WALTHER SPRING (*Rec. trav. chim.*, 1904, 23, 1—15).—In a previous communication (Abstr., 1884, 256), the author has shown that lead, zinc, ammonium sulphate, and ammonium alum, when strongly compressed, exhibit a diminished density. These observations have been extended to various metals by Kahlbaum, Roth and Siedler (Abstr., 1902, ii, 259), and to steel by Grunmach (*Ann. Phys. Chem.*, 1889, 67, 227). It is now shown that specimens of lead, tin, cadmium, and silver which have been forced through small apertures under pressure exhibit slight diminutions from the normal densities of these metals, whereas bismuth, similarly prepared, shows an increase in density. Further, when two plates of the same metal, one having been compressed and the other being the metal in the normal condition, are simultaneously placed in an electrolyte, a slight permanent current is produced, in one direction with the first four metals, which expand on liquefaction, and in the opposite direction for bismuth, which contracts when liquefied. Other slight changes in physical properties are also induced by strong compression.

The author suggests that these changes in density are due to the assumption by these substances under compression of the molecular condition characteristic of the liquid state. T. A. H.

[Phase Rule.] ALFRED BYK (*Zeit. physikal. Chem.*, 1904, 47, 223—227. Compare this vol. ii, 16).—A reply to Wegscheider (this vol., ii, 112). J. C. P.

Elementary Demonstration of the Phase Rule. C. RAVEAU (*Compt. rend.*, 1904, 138, 621—623).—A theoretical paper, unsuitable for abstraction. M. A. W.

Simple Proofs of the Phase Rule. AUGUSTE PONSOT (*Compt. rend.*, 1904, 138, 690—693).—It is shown that the phase rule can be proved in three ways. Firstly, by considering the osmotic pressure exerted by each component in a fluid medium which is separated from the phase by a semi-permeable membrane; secondly, when the volume concentration of each component and the temperature of equilibrium are given; and thirdly, from the equilibrium temperature and the vapour tensions of the components. S. S.

Thermometric Analysis of Solid Phases. E. S. SHEPHERD (*J. Physical Chem.*, 1904, 8, 92—115).—Bancroft has indicated a method for the determination of the composition of solid phases and the investigation of a three component system (*Abstr.*, 1902, ii, 495). The author has applied this method in an examination of the results of Heycock and Neville on the freezing points of alloys of gold, cadmium, and tin (*Trans.*, 1891, 936). In many cases, the temperatures, however, are not freezing points, but those at which a *second* solid phase appears. Numerous diagrams are given and many references to the original paper. The examination indicates the existence of a quintuple point at 20.9° , where the phases AuCd , AuCd_3 , Sn, liquid, and vapour co-exist, and a second quintuple point at 18.74° where the phases are Au, AuCd , Sn, liquid, and vapour. By extrapolation along different division lines, the composition of the fused mass at each of these quintuple points is approximately obtained. The various fields where 2 solid phases co-exist are determined as far as possible and indicated in the diagrams. The determinations of the composition of the solid phases by Bancroft's method indicate the existence of 2 alloys represented by the formulæ AuCd and AuCd_3 ; the second of these was not suspected by the original authors. No ternary compound of the three elements is indicated. L. M. J.

The Properties of the Curves representing the Indifferent States. E. ARIÈS (*Compt. rend.*, 1904, 138, 806—809. Compare *Abstr.*, 1903, ii, 589; this vol., ii, 16, 110).—A mathematical paper from which the following conclusion is drawn: the curves of the indifferent states of two systems the variabilities of which differ by unity are tangential to one another at those points indicating a temperature and pressure when they are both in an indifferent state, and capable of being derived the one from the other by the mere suppression or introduction of a determined phase. Thus, the indifferent state of a bivariant system can be considered as originating in a univariant state of $q+1$ phases by the suppression of a phase, and similarly the univariant state can be considered as taking its origin in an invariant state. M. A. W.

Conception of Independent Components. JOHANNES J. VAN LAAR (*Zeit. physikal. Chem.*, 1904, 47, 228—230. Compare *Abstr.*, 1903, ii, 536).—A reply to Wegscheider's criticism (this vol., ii, 17). J. C. F.

Theory of Reaction Velocity in Non-homogeneous Systems.

WALTHER NERNST (*Zeit. physikal. Chem.*, 1904, 47, 52—55).—The author argues in favour of the view that at the common surface of two phases equilibrium is established with very great rapidity, and that what is actually measured is the rate of the subsequent diffusion throughout the phases. This principle, enunciated first by Noyes and Whitney (Abstr., 1897, ii, 479) in connection with a physical change, is now applied to chemical and electrochemical reactions. In such a case as the solution of magnesia in acids, it is assumed, in accordance with the foregoing, that the solution in immediate contact with the magnesia is saturated with this substance, and therefore slightly alkaline. The rate of solution of the magnesia is then simply the rate at which the acid diffuses to the common surface; if the acid is thoroughly stirred, the fall of concentration will be confined to a thin layer of the thickness δ , surrounding the solid magnesia. For a given temperature, a given apparatus, and a given rate of stirring, δ will be constant and may be determined once for all.

The same reasoning is applied to electrochemical cases, where the common surface is that of an electrode, and where the velocity of reaction (for example, the reduction of iodine) is determined by the rate of diffusion of the reacting substance towards the electrode. In order that the same formulæ may be valid as in the purely chemical cases, it is necessary that the concentration of the reacting substance at the electrode be kept very small, and this is effected by making the *E.M.F.* suitably large. Here also the stirring must be uniform and thorough.

In view of the part played by diffusion in such cases as the above, the author casts doubt on van't Hoff's method of determining the order of a reaction in non-homogeneous systems. J. C. P.

Velocity of Reaction in Non-homogeneous Systems.

ERICH BRUNNER (*Zeit. physikal. Chem.*, 1904, 47, 56—102).—Nernst's application (see preceding abstract) of Noyes' and Whitney's theory (Abstr., 1897, ii, 479. Compare also Bruner and Tolloczko, Abstr., 1901, ii, 10; 1902, ii, 62; 1903, ii, 470) to chemical and electrochemical reactions, as well as to purely physical changes in non-homogeneous systems, is subjected to an experimental investigation.

The author has first determined the rate of solution of benzoic acid in water, a cake of the acid (obtained by fusion) being supported in a porcelain crucible lid, and the surrounding water being thoroughly mixed by a screw stirrer revolving from 110—205 times per minute. The rate of solution is given by the value of A , which, for a given temperature and rate of stirring, $= v/\Delta t \cdot \log(C - c_1)/(C - c_2)$, where v is the volume of the solution, C the concentration of the saturated solution, c_1 and c_2 successive values of the concentration at an interval of time Δt . The value of A is proportional to $(n)^\frac{1}{2}$, where n is the number of revolutions made by the stirrer per minute. By this relationship it is possible to reduce the values of A obtained in different reactions with different values of n to a common basis.

According to the theory, the rate of solution of magnesium hydroxide in benzoic acid should be the same as that of benzoic

acid itself in water under equal conditions of temperature, apparatus, and stirring, for both depend on the same thing, namely, the rate of diffusion of the benzoic acid. The author finds an approximate agreement. More generally, the velocity of reaction should be independent of the nature of the solid substance, provided only that the concentration of the diffusing substance is practically zero at the surface of the former. In harmony with this, it is found that the rates of solution of basic magnesium carbonate, magnesium hydroxide, and magnesium itself in benzoic acid are approximately equal. Magnesium and magnesium hydroxide dissolve equally rapidly in hydrochloric acid; with marble, however, as the solid, A is about 40 per cent. greater. The velocity of electrolytic separation of hydrogen at a platinised platinum electrode from solutions of benzoic and hydrochloric acids containing excess of potassium chloride, is within certain limits equal to the rate of solution of magnesium hydroxide. The values of A obtained (1) for a solution of iodine made into a paste with gum tragacanth, (2) for the electrolytic reduction of iodine solutions at a platinum cathode, were as 3:4, both experiments being made in normal potassium chloride solution containing varying quantities of potassium iodide. In view of the irregular rate of solution of solid iodine, this result is regarded as satisfactory.

Comparison of the values of A for the solution of magnesium hydroxide in different acids in presence of their magnesium salts shows that they increase in the following series: benzoic, acetic, formic, hydrochloric acids. If these acids were arranged according to the magnitude of their diffusion coefficients, the order would be the same as that just given. That benzoic acid dissolves magnesium hydroxide more slowly than acetic acid, although it is the stronger acid, is a fact in favour of the diffusion theory.

The value of δ (see Nernst, preceding abstract), as calculated from the author's experiments at 20°, varies from 0.018—0.052 mm. when the stirrer revolves 150 times per minute. A few experiments showed that the value of A at 30° was one and a half times greater than the corresponding value at 20°. As the temperature rises, δ diminishes, in virtue of the lower viscosity of the solutions. J. C. P.

A Reaction the Rate of which is Diminished by Rise of Temperature. CLARA C. BENSON (*J. Physical Chem.*, 1904, 8, 116—121).—Some of the author's former experiments on reactions in solutions containing chromic acid, potassium iodide, and ferrous sulphate (Abstr., 1903, ii, 200) had indicated that the rate of liberation of iodine was less at 30° than at 0°. This is further investigated and verified, whilst the experiments indicate that the course of the reaction is similar in both cases, being proportional to the first power of the concentrations of the iodide and ferrous salt and to the 1.7th power of that of the dichromate.

The author suggests two possible explanations, but has not made experiments to test the validity of either. L. M. J.

Determination of Avidity by the Polarimetric Method. JAMES WALKER (*Zeit. physikal. Chem.*, 1903, 46, 30—36).—The

rotation of an approximately seminormal solution of *l*-mandelic acid is -22.70° , that of the equivalent solution of sodium mandelate is -17.07° . The free mandelic acid is dissociated to about 3 per cent., and when this is repressed to 0.4 per cent. by adding hydrochloric acid, the rotation is -22.92° . The rotation of a solution containing the same equivalent quantities of mandelic acid and sodium acetate is -18.07° . Hence the sodium is distributed between the acetic and mandelic acids in the ratio 0.206:1.0; this agrees closely with the square root of the ratio of the dissociation constants of the two acids. The method has been tested, also with satisfactory results, for the case in which the inactive acid (malonic) is stronger than the active acid (*l*-mandelic). Using *l*-mandelic acid as a standard, the relative strength of the two inactive acids, acetic and malonic, may then be calculated. By applying this polarimetric method, it may be shown that whilst the primary dissociation constant of malonic acid is greater than that of tartaric acid, the second carboxyl group of malonic acid is much weaker than the second carboxyl group of tartaric acid, in accordance with Ostwald's theory (compare also Smith, *Abstr.*, 1898, ii, 284).

J. C. P.

Equilibrium between Iron, Ferrosoferric Oxide, Hydrogen, and Water Vapour. GERHARD PREUNER (*Zeit. physikal. Chem.*, 1904, 47, 385—417).—The furnace used was a protected magnesia tube, heated electrically, and inside this was put the porcelain tube in which the reaction took place. Two glass bulbs, containing water and communicating with one another, were connected with the porcelain tube, one at each end. There were also connected a tube to admit of evacuation or admission of hydrogen, and a manometer. The whole apparatus was mounted on a rocking scaffold immersed in water of a constant temperature, the effect of the rocking being to cause a circulation of the gases through the porcelain tube, and thus to secure a more rapid and trustworthy establishment of equilibrium.

According to the equation $3\text{Fe} + 4\text{H}_2\text{O} \rightleftharpoons \text{Fe}_3\text{O}_4 + 4\text{H}_2$, p_1/p_2 , where p_1 is the water vapour pressure after equilibrium has been reached, and p_2 the hydrogen pressure under the same conditions, should be a constant for a given temperature. This was found to be the case at three temperatures, 900° , 1025° , and 1150° , the mean values of p_1/p_2 being 0.69, 0.78, and 0.86 respectively. In these experiments, p_1 was varied between 8.8 and 49.3 mm., a considerably wider range than was found practicable by Deville, who investigated the equilibrium conditions of the same reaction.

The heat effect of the reaction $3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4\text{H}_2$, obtained by inserting the values of the equilibrium constants in van't Hoff's equation, is calculated to be 11,900 cal. at 960° , whilst calculation from calorimetric data gives 42,890 cal. When used in calculating the heat of formation of ferrosoferric oxide, the value 11,900 cal. gives a result much more in harmony with Baur and Glaessner's work (*Abstr.*, 1903, ii, 423) than does the value 42,890 cal.

J. C. P.

Law of Action of Maltase. Influence of the Concentration of Maltose. E. F. TERROINE (*Compt. rend.*, 1904, 138, 778—779). The velocity of hydrolysis of maltose by maltase (taka-diastrase) has

been determined by measuring the reducing power of the liquid on Fehling's solution, and also polarimetrically. The influence of the concentration of the maltose is expressed in the formula $v = K.a/(1 + ma)$, where v is the velocity of hydrolysis, a the concentration of maltose (0.5 to 10 per cent.), K and m two constants depending on the conditions of the experiment and of the ferment. The same law obtains in the cases of invertin, emulsin, amylase, and trypsin (compare Henri, Abstr., 1902, ii, 127; 1903, i, 304, 591, 643; ii, 135).

M. A. W.

Action of Maltase. Stability of the Ferment. CH. PHILOCHE (*Compt. rend.*, 1904, 138, 779—781).—Preparatory to the study of the kinetics of the reversibility of the enzyme action of maltase (compare Hill, Trans., 1898, 73, 634), the stability of the ferment during the time of the reaction has been determined by measuring the velocity of hydrolysis by maltase of solutions of equal sugar content, but containing different proportions of maltose and dextrose. It was found that the velocity of hydrolysis of a solution containing maltose, 4 per cent., and dextrose, 2 per cent., is the same as that of a 6 per cent. solution of maltose which has been acted on by the ferment for 24 hours; it follows, therefore, that the activity of maltase (taka-diastase) at 40° does not change during the first 24 hours.

M. A. W.

Theory of Catalytic Reactions. HANS EULER (*Zeit. physikal. Chem.*, 1904, 47, 353—356. Compare Abstr., 1900, ii, 532; 1901, ii, 57).—A criticism of Kullgren's recent paper (Abstr., 1903, ii, 535). In studying the influence of acids on the rate of inversion of sucrose, account must be taken of the dissociation of sucrose, either (1) into a laevulose ion and a dextrose ion, or (2) into the cation, $C_{12}H_{21}O_{10}^+$, and the anion, OH^- . A fuller treatment of the subject is promised.

J. C. P.

Palladium Catalysis of Hydrogen Peroxide. GEORG BREDIG and MAX FORTNER (*Ber.*, 1904, 37, 798—810).—The temperature employed was 25°, the hydrogen peroxide was titrated with permanganate, and the colloidal palladium was prepared by electrical powdering of palladium wire under $N/1000$ sodium hydroxide. The action is unimolecular and obeys a simple logarithmic law, but different preparations of palladium of the same concentration vary considerably in their activity. The catalytic action of the palladium (in presence of $N/60$ sodium hydroxide and $N/10$ hydrogen peroxide) can be distinctly noticed when the concentration of the palladium is only 1 gram atom to 26 million litres of solution.

Alkalis have an accelerating effect which reaches a maximum at intermediate dilutions, as is shown by the following table, which gives the times t_{50} for 50 per cent. decomposition at different concentrations:

| | $N/100000$ Pd + $N/10$ H_2O_2 | | | | | |
|--------------------|---------------------------------|---------|---------|----------|----------|-----------|
| + NaOH. | N . | $N/2$. | $N/4$. | $N/16$. | $N/64$. | $N/256$. |
| t_{50} (minutes) | 48 | 28 | 15 | 10 | 19 | 33 |

In acid solutions, the decomposition is exceedingly slow.

Hydrogen considerably increases the activity of the palladium; in one experiment, the amount of decomposition in 18 minutes was increased from 25 to 96 per cent. by bubbling a little purified hydrogen through the colloidal palladium suspension. This effect is much too great to be due to oxidation of the absorbed hydrogen by hydrogen peroxide, and must depend on some alteration in the surface of the palladium. Prolonged action of hydrogen coagulates the palladium, with formation of a hydrogen alloy, but when this is oxidised again by hydrogen peroxide, the palladium or its oxide obtained is naturally in a still finer state of division, and the active surface therefore increased. Carbon monoxide at first retards and then greatly accelerates the catalytic action of the palladium; this is explained as being due to the "poisoning" of the metal by carbon monoxide and subsequent oxidation to carbon dioxide, leaving the metal in a state of increased activity.

Iodine acts as an anticatalyst; the addition of $N/107$ iodine to $N/13200$ palladium reduced the velocity of decomposition by 25 per cent. Hydrogen sulphide has a retarding effect, probably owing to the conversion of palladium metal into sulphide and mercuric chloride; hydrogen cyanide and hydrogen arsenide have a somewhat similar effect.

T. M. L.

Catalysis of Hydrogen Peroxide by Iodine Ions. JAMES HENRI WALTON, jun. (*Zeit. physikal. Chem.*, 1904, 47, 185—222).—A method has been worked out whereby it is possible to measure at intervals the oxygen that has been evolved from a mixture of potassium iodide and hydrogen peroxide solutions, and thus to determine the rate of decomposition of the peroxide. The decomposition proceeds as a reaction of the first order, and the velocity is proportional to the concentration of the iodine ions, as shown by experiments with potassium, sodium, ammonium, and cadmium iodides. Hence the addition of any substance (such as iodine or mercuric iodide) which removes iodine ions by forming complexes retards the catalysis. On the supposition that potassium tri-iodide is catalytically ineffective, it is possible to calculate the amount of free iodine in close agreement with Jakowkin (*Abstr.*, 1894, ii, 271; 1896, ii, 514). Addition of alkali retards the decomposition of hydrogen peroxide by iodine ions, and the order of the reaction is altered. The influence of normal salts, such as potassium chlorate, nitrate, sulphate, chloride, sodium sulphate and chloride, on the catalysis is only slight. The formation of iodate or periodate as an intermediate product of the catalysis is improbable, since neither salt intensifies the catalytic effect of potassium iodide on the decomposition. On the other hand, it is probable that hypoiodite is formed as an intermediate product, although from conductivity and freezing point experiments it appears that the quantity of hypoiodite present at any moment is relatively small. The velocity of the catalysis is approximately doubled for a rise of 10° in temperature.

J. C. P.

Indicators for Acids and Alkalis. W. SALESSKY (*Zeit. Elektrochem.*, 1904, 10, 204—208).—The potential difference between two

hydrogen electrodes is measured. The one electrode dips into normal hydrochloric acid, the other into a solution of the indicator, to which acid or alkali is added until the change of colour just takes place. By means of Nernst's formula for the *E.M.F.* of a concentration cell, the concentration of the hydrogen ions in the indicator solution is readily calculated.

The following table contains the results obtained. The concentrations are given in gram-equivalents per litre.

| Indicator. | Concentration of hydrogen ions. | Indicator. | Concentration of hydrogen ions. |
|------------------|---------------------------------|-----------------|---------------------------------|
| Methyl-violet | 2×10^{-3} | Methyl orange | 1.4×10^{-5} |
| Benzopurpurin B. | 5×10^{-4} | „ yellow | 1×10^{-7} |
| Fluorescein | 4.2×10^{-4} | Turmeric | 1.4×10^{-7} |
| Gallein | 6.3×10^{-5} | Phenolphthalein | 1×10^{-7} |
| Congo-red | 6×10^{-5} | „ red | 3.2×10^{-9} |
| Rosolic acid | 5.4×10^{-5} | Curcumin W. | 4.8×10^{-8} |
| Alizarin | 3.6×10^{-5} | Tropæolin 000 | 1×10^{-8} |
| | | Litmus, red | 1×10^{-5} |
| | | „ blue | 1×10^{-8} |

In most cases, the concentration of the hydrogen ions at which the colour change occurs does not depend on the concentration of the indicator. Methyl orange is an exception; the larger concentration was found for 1/20000 to 1/500000*n* solutions, and the smaller value for 1/4000 to 1/6000*n* solutions. T. E.

Indicators for Acids and Alkalis. BRUNO FELS (*Zeit. Elektrochem.*, 1904, 10, 208—214).—Referring to Salesky's work (preceding abstract), the author points out that a ten-fold increase in the concentration of the hydrogen ions in the concentration cells measured only increases the *E.M.F.* by 0.058 volt; it is therefore desirable to test the accuracy of the results by another method. When a solution of a salt of a weak base or acid is mixed with a solution of the free base or acid, a solution is obtained in which the concentration of the hydrogen ions can be calculated from the known dissociation constants of water and of the base or acid. The concentration of the hydrogen ions in such solutions is practically unaffected by the presence of traces of impurities in the water and salts used, which is very far from being the case with very dilute solutions of strong acids or alkalis. Many of the results obtained by Friedenthal (this vol., ii, 288) are uncertain owing to the latter circumstance. The solutions used are (a) mixtures of ammonia and ammonium chloride, $[H^+] = 10^{-8}$ to 10^{-10} ; (b) sodium acetate and acetic acid, $[H^+] = 10^{-4}$ to 10^{-6} ; (c) sodium phthalate saturated with phthalic acid, $[H^+] = 10^{-2}$ to 10^{-4} ; sodium *p*-nitrophenol saturated with *p*-nitrophenol, $[H^+] = 10^{-7}$ to 10^{-8} . Curves are given showing the connection between the composition of the solutions and the concentration of the hydrogen ions. By means of these solutions, the exact concentration of hydrogen ions at which the change of colour of the indicator occurs is easily found (with the yellow phenol solutions, the spectroscope was used). The results obtained are as follows:

| Indicator. | Colour change. | Concentration of hydrogen ions [H ⁺]. |
|-----------------------|-----------------------------|---|
| Tropæolin 000 | Orange to red | $10^{-11.2}$ |
| Phenolphthalein | Red | $10^{-7.76}$ |
| " | Colourless | $10^{-7.50}$ |
| Curcumin W. | Red | $10^{-7.62}$ |
| Litmus | Blue to red | $10^{-6.97}$ |
| <i>p</i> -Nitrophenol | Yellow | $10^{-6.74}$ |
| " | Colourless | $10^{-6.13}$ |
| Methyl-orange | Yellow | $10^{-5.23}$ |
| " | Orange | $10^{-4.07}$ |
| " | Red | $10^{-3.3}$ |
| Congo-red | Red to intermediate colour | $10^{-4.41}$ |
| " | Blue to intermediate colour | $10^{-3.76}$ |
| Methyl-violet | Violet | $10^{-2.38}$ |
| " | Blue | $10^{-2.05}$ |

The results agree fairly well with those obtained by Salessky. It is pointed out that, within the usual limits, the concentration of the indicator does not affect the point at which the colour change takes place. The colour of a methyl-orange solution remains practically unchanged over a fairly wide range of concentrations, hence its indications are not very sharp. The concentration of the hydrogen ions in a neutral solution is about 10^{-7} , which is the concentration of the hydrogen ions in pure water. T. E.

Solubility and Size of Grain. GEORGE A. HULETT (*Zeit. physikal. Chem.*, 1904, 47, 357—367. Compare Ostwald, Abstr., 1900, ii, 712; Hulett, Abstr., 1901, ii, 493).—By way of reply to Kohlrausch (Abstr., 1903, ii, 528), the author confirms and supplements his earlier experiments on the variation in the solubility of calcium and barium sulphates with the state of division of the solids. In general, the influence of the size of grain on the solubility of a substance is negligible when the solubility exceeds 2 per cent. The increase of the normal solubility that may be temporarily observed by using finely divided solid amounts to 20 per cent. in the case of calcium sulphate, and 80 per cent. in the case of barium sulphate. J. C. P.

[**Solubility and Size of Grain.**] FRIEDRICH KOHLRAUSCH (*Zeit. physikal. Chem.*, 1904, 47, 625—626).—A reply to Hulett (preceding abstract). J. C. P.

Influence of Temperature on the Solubility of Certain Compounds in Sulphur Dioxide. MIECZYSLAW CENTNERSZWER and I. TELETOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 62—71).—The authors have examined the solubilities, at different temperatures, of anthracene, anthraquinone, and quinol in liquid sulphur dioxide. The substance was heated with the dioxide in a thick-walled, sealed, glass tube, which was well shaken and the temperature noted at which the solid disappeared. At high temperatures, the solubilities increase very quickly, the curves being approximately asymptotic to lines parallel to the axis of solubility. On

increasing the concentration of the solution by 1 per cent., its critical temperature is raised by 5° , so that, with these three substances, the solubility becomes infinitely greater before the critical temperatures of their saturated solutions are reached. The authors denote by "mean solubility" the relation $(s + \sigma)/(l + \lambda)$, where s and σ denote the quantities of the substance dissolved in the liquid sulphur dioxide (of weight l) and the vapour (of weight λ) respectively. By calculations based on the phase rule, the conclusion is arrived at that the mean solubility of any difficultly volatile substance is not a constant magnitude at any particular temperature, but increases with an increase in the proportion of the tube filled with the liquid.

Taking a tube filled to a certain fraction (0.26) of its volume with liquid sulphur dioxide, it is found that, if the concentration of anthraquinone is less than a certain limit (8.8 per cent.), the temperature of complete solution lies below that at which the meniscus disappears. If, however, the concentration of the anthraquinone solution in the tube equals or exceeds 8.8 per cent., the following four definite temperatures are observed: (1) Temperature at which the meniscus first disappears. (2) Temperature of re-appearance of the meniscus. (3) Temperature of complete solution. (4) Temperature of the second disappearance of the meniscus. This phenomenon is one of "retrograde condensation" (condensation on heating and evaporation on cooling) taking place in a system of three phases and with a constant volume for the whole system. If 0.35 of the volume of the tube is filled with solution, similar retrograde condensation is observed, but this is not the case when the liquid occupies 0.41 or 0.51 of the enclosed volume, the temperature of complete solution then lying well below that at which the meniscus disappears. When the fraction reaches 0.61, the meniscus disappears at the upper end of the tube; if the concentration is less than 17 per cent., the temperature of solution is lower than that of the disappearance of the meniscus, but if more than 17 per cent. of the anthraquinone is present in the solution, the meniscus disappears at a lower temperature than that of complete solution.

T. H. P.

Apparatus for the Determination of the Solubility of Salts in Liquids other than Water and at Temperatures above 100°
H. CANTONI (*Ann. Chim. anal.*, 1904, 9, [iii], 81—83).—A modification of Durand's apparatus. It consists of a receiver made of Jena glass of 1250 c.c. capacity. The large neck is fitted with a doubly-perforated rubber cork, one hole of which is eccentric. Through the central opening passes the tube of a condenser, in which rotates freely the stem of a stirrer; this dips into the receiver and agitates the suspended substance the degree of solubility of which must be determined.

Through the eccentric hole passes a glass tube communicating with a small porcelain hollow cylinder of 50—60 mm. diameter, which dips into the receiver. The lower part of this cylinder is perforated with several small holes. In the interior of this tube is placed a plug of glass-wool, then some asbestos up to the height of the perforated part. This arrangement serves as a filter.

The whole is immersed in a bath furnished with a stirrer, a thermometer, and, at the bottom, with a semi-cylindrical chamber with an internal tubulus, through which passes the stem of a glass siphon; this communicates with the porcelain cylinder which dips into the liquid and serves as a filter.

The bath is filled with oil so as to readily obtain temperatures above 100°. The central stirrer constantly keeps this oil in motion, causing an equal temperature throughout the bath. The temperature is kept constant by means of a mercury-regulator.

The different stirrers are kept going by means of an electric motor. At the end of the operation it is sufficient to set the siphon going by means of an aspirator to collect the different solutions, which are then analysed.

Three operations may be conducted at the same time. A full illustration of the apparatus is given. L. DE K.

Method of Stating the Concentration of Solutions. HARTOG J. HAMBURGER (*Zeit. physikal. Chem.*, 1904, 47, 495—496).—In an electrolytic solution, the dissolved units comprise both molecules and ions, whilst the concentration as usually stated refers only to the total number of molecules. The author, from the standpoint chiefly of the physiologist and pathologist, shows the need for such a term as “osmotic concentration,” indicating by this the number of gram-molecules + gram-ions per litre of solution. As a contraction for the phrase “gram-molecules + gram-ions,” he proposes the word “molions.” The concentration of a solution as thus stated is directly deducible from its freezing point. J. C. P.

The Amide Group. CHARLES E. FAWSITT (*Proc. Roy. Soc. Edin.*, 1904, 25, 51—60. Compare Abstr., 1903, ii, 15).—The viscosity of aqueous solutions of (1) carbamide, (2) acetamide, varies as required by the formula $\eta_x = A^x$, where A is a constant and η_x the viscosity at the concentration x . The author cannot confirm Rudolf's statement (Abstr., 1903, ii, 403) that carbamide in dilute aqueous solution shows a negative viscosity.

The molecular conductivity of hydrochloric acid, to which gradually increasing quantities of carbamide have been added, diminishes rapidly; the molecular conductivities of potassium chloride and sodium hydroxide under the same conditions are diminished only to a slight extent, which is about the same for each electrolyte. It may therefore be concluded that amides do not possess any acidic character, and that their general formula is $O:CR \cdot NH_2$ rather than $OH \cdot CR : NH$.

The viscosities and conductivities of a potassium chloride solution to which increasing quantities of carbamide have been added are found on comparison to be very closely related.

The non-conductivity of amides in aqueous solution is a good criterion of their purity. J. C. P.

Separation of Solids in the Surface Layers of Solutions and Suspensions. (Observations on Surface Membranes, Bubbles, Emulsions, and Mechanical Coagulation.) W. RAMSDEN (*Proc. Roy. Soc.*, 1903, 72, 156—164).—In continuation of his previous

experiments (Abstr., 1895, i, 254), the author has found that, apart from evaporation, solid or highly viscous coatings are spontaneously formed on the free surfaces of all proteid solutions, of many non-proteid colloid solutions, of fine and coarse suspensions, and of a few apparently crystalline solutions. Similar coatings are formed at the common surface of two liquids, which, without being highly viscous, form persistent emulsions. The explanation of such a separation of previously dissolved matter at the free surfaces of solutions is sought in the observation that all solutes which so accumulate, lower the surface tension of water. The accumulation of solid or highly viscous matter on the surface of their solutions has been shown for a large number of substances by (1) the formation of mechanical surface aggregates, (2) the occurrence of intense special superficial viscosity, or (3) the formation of persistent bubbles. There is very considerable parallelism in the three phenomena. J. C. P.

Reciprocal Pairs of Salts. WILHELM MEYERHOFFER (*Ber.*, 1904, 37, 1116—1120. Compare this vol., ii, 170).—A reply to Witt and Ludwig (*ibid.*, ii, 171). The author makes use of the phase rule, and concludes that the solution plays no part, but that the reactions occur between the solids. J. J. S.

Mutual Relationships of Colloids in Solution. WILHELM BILTZ (*Ber.*, 1904, 37, 1095—1116. Compare Picton and Linder, *Trans.*, 1897, 71, 572; Lottermoser, *Ahren's Sammlung*, 1901, 76; Spring, *Abstr.*, 1900, ii, 713).—Directions are given for the preparation of colloidal solutions of platinum, gold, selenium; of cadmium, antimony, and arsenic sulphides; of silicic acid, stannic acid, molybdenum oxide, Mo_3O_8 , tungsten blue, vanadium pentoxide, and hydroxides of cerium, zirconium, thorium, chromium, aluminium, and iron (Abstr., 1903, ii, 153). All the hydrosols, with the exception of the hydroxides, are attracted towards the anode. When a current is passed through the colloidal solution, the hydroxides mentioned above, on the other hand, are attracted towards the cathode. It appears that hydroxyl compounds are positively charged, but the other colloids negatively.

Oppositely charged hydrosols are able to precipitate one another in the absence of an electrolyte, and the precipitate obtained consists of a gelatinous mass of the two hydrosols (*adsorption compounds*). Hydrosols with similar charges cannot precipitate one another except in the presence of an electrolyte. Even with oppositely charged hydrosols, precipitation only occurs within certain limits of concentration. If the solutions are too concentrated or too dilute, no precipitate is formed.

The fact that the power of precipitation of negatively charged colloids by salt solutions increases considerably with the valency of the cation of the salt employed (Schulze, *Abstr.*, 1882; Linder and Picton, *Abstr.*, 1895, 67, 63; Freundlich, *ibid.*, 1903, ii, 532) is in perfect harmony with the view that the precipitation is caused by the presence of colloidal metallic hydroxides in the aqueous solutions of the salts. The same generalisation does not apply to positively charged

hydrosols; for example, five c.c. of colloidal ferric hydroxide solution were mixed with 0.5 mol. normal solution of different salts with the following results: Potassium chloride, after 2 hours, slight turbidity. Barium chloride, after 1 hour, copious turbidity. Aluminium chloride, after 2 days, no turbidity. J. J. S.

Colloidal Solutions. Application of the Phase Rule to the Precipitation of Colloids. VICTOR HENRI and ANDRÉ MAYER (*Compt. rend.*, 1904, 138, 757—760).—The phase rule can be applied to the study and systematic classification of the conditions of precipitation of colloidal solutions, whether such solutions are regarded as consisting of two phases, namely, small granules suspended in a liquid, or of one phase; the precipitation of (1) colloidal copper ferrocyanide by copper nitrate; (2) colloidal silver by colloidal ferric hydroxide; and (3) proteid substances by acids, copper, or silver salts, are all reversible reactions, the precipitate dissolving in the excess of the reagent. Further, it is possible in the case of a proteid and copper sulphate for certain concentrations to obtain a system of three phases: copper sulphate crystals, precipitated albumin *plus* copper, and a solution of albumin and copper sulphate; if the proportion of albumin is increased, the composition of the solution changes, and in accordance with the phase rule the composition of the precipitate also changes. Mixtures of gelatin, water and sodium chlorate, or gelatin, water and sodium chlorate, or gelatin, water and copper sulphate behave similarly, giving rise to systems of two or three phases.

M. A. W.

The Coagulation of Colloidal Solutions. JACQUES DUCLAUX (*Compt. rend.*, 1904, 138, 809—810. Compare this vol., ii, 162, 243).—The electropositive radicles differ greatly in the ease with which they replace chlorine in colloidal ferric hydroxide $[\text{Fe}_2(\text{OH})_m\text{Cl}_n]$; hydroxyl is the most active, and the bivalent are much more active than the univalent radicles; thus the displacing power of sulphuric is at least 20 times as great as that of nitric acid, or, in other words, in order to coagulate a given volume of the colloidal solution, it would require a much larger quantity of hydrochloric or nitric than of sulphuric acid. The coagulation is accompanied by a definite change in the composition of the solution which is independent of the nature of the acid. This chemical modification is to be regarded as the cause of the coagulation, for there exists initially a state of chemical equilibrium between the particles of the colloid and the surrounding liquid; the addition of different salts in quantities inversely proportional to their displacing power modifies the composition of the two phases to the same extent, and it follows that when the system has been displaced to a certain extent from its original state of equilibrium, coagulation will set in.

M. A. W.

Solution and Swelling ("Quellung?") of Colloids. KARL SPIRO (*Beitr. chem. Physiol. Path.*, 1904, 5, 276—296. Compare this vol., i, 124; Pauli, *Abstr.*, 1902, ii, 388; 1903, i, 299; Zsigmondy, *Zeit. Elektrochem.*, 1902, 8, 684).—Hydroxyl and hydrogen ions and colloidal

ferric hydroxide solution all accelerate the "swelling" of gelatin, even in the presence of a third substance like dextrose. With dextrose alone, the maximum value is obtained with a 3 per cent. solution. With a 25 per cent. solution of dextrose, practically no water is absorbed, and with still more concentrated solutions the gelatin contracts owing to loss of water.

Milk (dialysed), serum albumin, and colloidal arsenious sulphide do not accelerate "swelling." Other substances, for example, agar plates, are not affected in the same manner as gelatin by colloids. There is no close relationship between swelling and osmotic pressure, and there is no hard and fast line between colloids and crystalloids, as certain colloids (for example, egg albumin) can diffuse through plates of gelatin.

Colloidal ferric hydroxide solution, obtained by prolonged dialysis, is a complex material and contains appreciable amounts of chlorine in solution. Part of the substance is undoubtedly present in true solution, but the greater part is merely in fine suspension. Solutions obtained by prolonged dialysis are far less active than commercial solution on gelatin.

The presence of a small amount of an electrolyte in solution appears to be necessary for the formation of a colloidal solution. J. J. S.

Theory of Pseudo-acids. HUGO KAUFFMANN (*Zeit. physikal. Chem.*, 1904, 47, 618—624. Compare Hantzsch, *Abstr.*, 1899, i, 399; Hantzsch and Barth, *Abstr.*, 1902, i, 222).—According to Hantzsch, one characteristic of a pseudo-acid is that the hydrolysis of the sodium salt has a smaller value than that calculated from the dissociation constant of the free acid. The author's theoretical investigation shows that the law of mass action furnishes no basis for this method of characterising pseudo-acids, and it is found that the hydrolysis of the salts of a pseudo-acid must be as great as that of the salts of an ordinary acid with an equal dissociation constant. The cases of abnormally low hydrolysis, established by Hantzsch's experiments, are probably connected with incomplete electrolytic dissociation of the salts, or with some other factor, the importance of which has not yet been recognised. J. C. P.

Polymerisation of Orthomeric Liquids, Especially of Acetic Acid. ALEXIUS J. BATSHINSKI (*Chem. Centr.*, 1904, i, 868; from *Bull. Soc. Imp. Naturalistes Moscou*, 1903, 188—199).—A method of determining the degree of polymerisation of liquids, the vapours of which have the same degree of complexity ("orthomeric" liquids), has already been devised (*Abstr.*, 1902, ii, 444). This method has been applied to the case of acetic acid, methyl formate and fluorobenzene serving as standard substances. The results obtained varied somewhat with the method of calculation employed and the compound chosen for the standard, but were on the whole fairly concordant. The differences are due to the slight polymerisation of the standard substance itself or to the insufficient accuracy of the determination of its critical volume, and to the fact that the law of coincident conditions is not absolutely true. The mean values obtained for

the degree of polymerisation are at 100° 1.7, at 150° 1.6, at 200° 1.5, at 250° 1.4, and at 300° 1.3; they are a little lower than those found by Ramsay and Shields, and lie, on the whole, between those found by other observers. E. W. W.

Size of the Molecules of Compounds in the Liquid State. WILHELM VAUBEL (*J. pr. Chem.*, 1904, [ii], 138—144).—The author has calculated the association factor of a number of liquid elements and compounds, both inorganic and organic: by his own method, from the heat of vaporisation and the "gravitation factor"; by Ramsay and Shields' method, from the surface tension; by Traube's method, from the co-volume; and by Longinescu's method, from the absolute boiling point and the density. The results are tabulated. The different methods "on the whole lead nearly always to an approximately correct value." C. F. B.

Theoretical Considerations Respecting the Origin and Essence of the Chemical Elements. WILLIBALD HENTSCHEL (*J. pr. Chem.*, 1904, 69, 187—192).—In the light of recent discoveries with regard to radioactivity, the author discusses his idea, enunciated fifteen years ago, that "matter may be regarded as an accumulation of radiant energy." C. F. B.

Distribution of Elements in the Earth in Relation to their Atomic Weights. LOUIS DE LAUNAY (*Compt. rend.*, 1904, 138, 712—714).—It is suggested, on geological grounds, that the original distribution of the elements in the earth at the time of its fluidity was, from the exterior towards the centre, approximately in the order of their atomic weights, their distance from the centre being greater the smaller the atomic weight. This is the order the atoms, free from all chemical affinity at such high temperatures, would assume as a result of rotation of the fluid mass. L. J. S.

Apparatus for Regulating the Action of Vacuum Pumps. JEAN MEUNIER (*Compt. rend.*, 1904, 138, 693—694).—A valve made from a perforated glass tube covered with a rubber band is inserted between the vacuum pump and the exhausted vessel. This arrangement serves to prevent water being sucked back from the pump during changes in the flow of the current. S. S.

New Forms of Pipettes. B. M. MUKERJEE (*Chem. News*, 1904, 89, 161).—Two pipettes are described for use in drawing up bromine, chlorine water, &c. In the first, the upper tube of an ordinary pipette is bent at a right angle and enters the top of a reservoir filled with water. A tube passes to the bottom of this reservoir, and has near the top a large bulb. The pipette is filled by drawing the water from the reservoir into this bulb. A valve may also be placed in the upper tube of the pipette for greater safety. The second example consists of a pipette with the tube above the mark bent into the shape of a U-tube, which is filled with water. W. P. S.

Inorganic Chemistry.

Formation of Solids at Low Temperatures, particularly with regard to Solid Hydrogen. MORRIS W. TRAVERS (*Proc. Roy. Soc.*, 1904, 73, 181—183).—The author has previously found that hydrogen remained liquid down to 14.2° (Helium scale), but solidified when the pressure fell to 49 or 50 mm. of mercury corresponding with a temperature of 14.1° , but no observations of its appearance were made. The experiments have been modified and repeated in order to determine whether the glassy substance described by Dewar is definite crystal or merely a highly viscous liquid. The author found that when the liquid hydrogen was made to boil in a vacuum the liquid did not appear to become viscous, and films of glassy substance formed at the surface and broke as the bubbles rose. The sharpness with which the solid hydrogen was formed and the constancy of the melting pressure lead the author to believe that the solid hydrogen is a crystalline substance and not a pseudo-solid.

L. M. J.

Density of Fluorine. HENRI MOISSAN (*Compt. rend.*, 1904, 138, 728—732).—The discrepancy between the experimental (1.260) and the theoretical value (1.316) for the density of fluorine (compare Abstr., 1890, ii, 208) led Brauner to suggest that the gas may be a mixture of atomic and molecular fluorine, a fact which would also account for its great chemical affinity (compare Trans., 1894, 65, 401). The author has therefore redetermined the density of the gas by the Regnault method, using a glass globe in place of the platinum vessel employed in the earlier investigation (compare Abstr., 1900, ii, 140). The glass globe was weighed full of nitrogen, and then full of fluorine, a correction being made for the residual nitrogen. The mean of four determinations gave the number 1.310 for the density of fluorine, a value so closely approximating to the theoretical (1.319), calculated from $F=19.05$, as to exclude the possibility of the existence of free atoms in gaseous fluorine.

M. A. W.

Preparation and Properties of Liquid Oxygen. ERNST ERDMANN and FRED BEDFORD (*Ber.*, 1904, 37, 1184—1193).—At -191.5° , liquid oxygen dissolves 458 times its volume, or 50.7 per cent. of its weight, of gaseous nitrogen; it is therefore necessary in preparing pure liquid oxygen to carefully exclude air.

E. F. A.

Composition and Temperature of Liquid Air. ERNST ERDMANN (*Ber.*, 1904, 37, 1193—1196).—Liquid air freshly drawn from the Hampson machine contains about 30 per cent. of oxygen and boils at about -194° .

E. F. A.

Physical Chemistry of the Lead Chamber Process. MAX TRAUTZ (*Zeit. physikal. Chem.*, 1904, 47, 513—610).—The reactions of

the lead chamber take place with such great rapidity that a final decision as to their relative importance cannot yet be reached.

The oxidation of sulphur dioxide in aqueous sulphuric acid solutions has been qualitatively studied. The rate of decomposition of nitrosulphonic acid at 25° in aqueous sulphuric acid of varying strength has been determined. In dilute sulphuric acid solutions, what is actually measured is the rate of escape of nitric oxide from a super-saturated solution, the hydrolysis of the nitrosulphonic acid taking place almost instantaneously; when the sulphuric acid is stronger, the rate of hydrolysis is lower, and is superposed on the rate of escape of the nitric oxide.

Nitric oxide acts on the system $\text{HNO}_3 + \text{H}_2\text{O} + \text{H}_2\text{SO}_4$, forming nitrosulphonic acid and nitrogen peroxide. So long as the percentage of the sulphuric acid is less than 52, the process is reversible at all temperatures between 22° and 82°. The partial pressure of the nitrogen peroxide produced in the foregoing reaction rises with increasing sulphuric acid concentration to a maximum, and then falls off until with 93 per cent. sulphuric acid it has a negligibly small value. There is produced at this concentration not only nitrosulphonic acid, but also nitrosodisulphonic acid the concentration of which is approximately proportional to the nitrogen peroxide concentration.

In the presence of nitric acid, nitric oxide can reduce sulphuric acid to sulphur dioxide—a process to be attributed to successive condensation and resolution (compare Raschig's theory).

Under the conditions of the lead chamber, a reaction takes place between nitrosodisulphonic acid and nitrous acid (also nitrosulphonic acid or its decomposition products), leading to nitric oxide and sulphuric acid; it is probable that this reaction is of considerable importance in the lead chamber process.

Nitrosodisulphonic acid, $\text{NO}(\text{SO}_3\text{H})_2$, has been prepared in several new ways, and it has been shown that this compound results from the reduction of nitrosulphonic acid by sulphur dioxide in concentrated sulphuric acid, the reduction being accelerated by heating.

It is pointed out that the usual method of determining the nitrogen acids in the chamber gases is faulty, and it is therefore probably not yet known with certainty which oxides of nitrogen predominate in the chamber.

The paper contains a detailed critical and historical review of the literature dealing with the theory of the lead chamber process.

J. C. P.

Catalysis of Hydrazine. ATTILIO PURGOTTI and L. ZANICHELLI (*Gazzetta*, 1904, 34, i, 57—87. Compare Tanatar, *Abstr.*, 1902, ii, 386 and 495).—Tanatar's equation, $3\text{N}_2\text{H}_4 = 4\text{NH}_3 + \text{N}_2$, for the catalytic decomposition of hydrazine sulphate by platinum black is confirmed. It is shown that platinum black, when boiled with water for four hours, quite loses its property of decomposing hydrazine sulphate, although still possessing normal catalytic power with regard to hydrogen peroxide and hydroxylamine; such platinum, after being used to decompose the latter two substances, has not regained its activity towards hydrazine. Platinum black which has been heated in a

current of hydrogen is similar, and platinum which has been precipitated by hydrazine or hydroxylamine from a solution of platinic chloride is also inactive as long as it remains suspended in the liquid in which it is formed; on filtering it, however, and drying it in the air, it regains its normal activity. The behaviour of platinum reduced from its chloride by alcoholic potash is similar, but it at once decomposes hydroxylamine and hydrogen peroxide. The authors consider that the catalysis of hydrazine is initiated by traces of oxygen occluded by the platinum; it is noteworthy that the inactive platinum, which can be rendered active by washing it with water and drying in the air, does not become active if kept in water through which air is bubbled for several hours or in which hydrogen peroxide is caused to decompose. The inactive platinum seems not to possess the power of absorbing oxygen whilst covered with water. From the foregoing observations, it is concluded that, contrary to Tanatar's views, the mechanism of the catalysis of hydrazine is totally different from that of the catalysis of hydroxylamine. Platinum which is inactive towards hydrazine sulphate is also inactive to hydrazine hydrate, a fact indicating the same mechanism to exist in both these cases, and again contrary to Tanatar's opinions.

From a study of catalysis of aqueous solutions of hydrazine sulphate, it is concluded that the velocity of decomposition increases nearly proportionately to the increase in the amount of platinum present, and roughly also to the increase of concentration.

The rate of decomposition by platinum of aqueous salts of hydrazine varies greatly with the nature of the acid; the monohydrochloride, sulphate, nitrate, and hydrobromide are most rapidly affected and in the order given, whilst the diacetate, dihydrochloride, and dihydrobromide are much less readily decomposed. It is shown that the addition of traces of acids has a very varying influence on the catalysis; sulphuric, hydrochloric, phosphoric, and boric acids have little effect, but hydrofluoric, hydrobromic, hydriodic, and nearly all organic acids very much retard, if they do not completely inhibit, decomposition. These facts, taken into account with their dissociation, explain the varying nature of the catalysis of hydrazine salts in solution.

W. A. D.

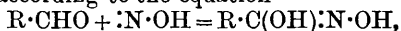
Hydroxamic Acids. ANGELO ANGELI and FRANCESCO ANGELICO (*Gazzetta*, 1904, 34, i, 50—57. Compare Abstr., 1902, i, 765; and this vol., ii, 115).—In preparing nitrohydroxylaminic acid from hydroxylamine, ethyl nitrate, and sodium ethoxide, the yield is never greater than 50 per cent. that of theory, owing to part of the ethyl nitrate being decomposed to form nitrous acid and acetaldehyde, the latter then combining with hydroxylamine to form acetaldoxime. The formation of the oxime was ascertained by its distilling with the alcohol used as solvent; it was hydrolysed, and the hydroxylamine formed converted into piperonaldoxime.

The difference between the decomposition of the silver salt and sodium salt of nitrohydroxylaminic acid (compare *loc. cit.*) is discussed; the sodium salt in aqueous solution is resolved into the ions, Na, Na and N_2O_3 , and ultimately gives NO_2 and NO. The insoluble silver salt

decomposes according to the equations (1) $\text{Ag}_2\text{N}_2\text{O}_3 = \text{AgNO}_2 + \text{AgNO}$, (2) $\text{AgNO} = \text{Ag} + \text{NO}$; it is shown experimentally that the ratio of silver formed to nitric oxide generated is approximately 1:1, as required by equation (2).

The oxidation of sodium nitrohydroxylamine by potassium permanganate in neutral solution takes place nearly quantitatively according to the equation $\text{Na}_2\text{N}_2\text{O}_3 + 3\text{O} = 2\text{NaNO}_3$.

Nitrohydroxylaminic acid is the only reagent which satisfactorily differentiates ketones from aldehydes; the hydroxamic acids produced from aldehydes, according to the equation



are distinguished by their characteristic behaviour with ferric chloride on copper acetate. As these hydroxamic acids are readily hydrolysed to the corresponding carboxylic acids, the use of nitrohydroxylaminic acid affords a ready means of transforming aldehydes into acids without resorting to destructive processes of oxidation. W. A. D.

Cause of the Conductivity of Air in which Phosphorus is Oxidised. F. HARMS (*Chem. Centr.*, 1904, i, 708; from *Physikal. Zeit.*, 5, 93—95).—The relationship of the number of oxidised oxygen molecules to the number of ions formed by the oxidation of phosphorus in air has been estimated. The latter was determined by measuring the strength of the saturation current, which is readily obtained by employing low oxygen pressures. An *E.M.F.* of 500—1200 volts was used and the progress of the action observed by means of a manometer. From the experimental data, it has been calculated that ions only begin to be formed after eight millions of oxygen molecules have taken part in the action. Ionisation is not, therefore, directly due to the process of oxidation, but depends rather on the formation of ozone by a secondary reaction (compare Richarz and Schenck, this vol., ii, 154). Ionisation does not appear to occur when phosphorus vapour is burnt in oxygen. E. W. W.

Some Physical Constants of Phosphorus Fluorides. HENRI MOISSAN (*Compt. rend.*, 1904, 138, 789—792).—The fusing points and boiling points of the phosphorus fluorides have been redetermined, using a thermoelectric couple instead of an ordinary thermometer, with the following results: phosphorus trifluoride, PF_3 (compare Abstr., 1885, 15, 482), melts at -160° and boils at -95° under atmospheric pressure; phosphorus pentafluoride, PF_5 (compare Thorpe, Abstr., 1877, 46; Moissan, Abstr., 1886, 303; 1887, 212), prepared by the action of arsenic fluoride on phosphorus pentachloride, forms a white, flocculent solid, melting at -83° to a colourless liquid which does not attack glass and boils at -75° ; phosphorus oxyfluoride, PF_3O (compare Abstr., 1886, 767; 1891, 264; and Thorpe and Hamels, Trans., 1889, 55, 759), forms a white, crystalline solid melting at -68° to a colourless liquid, which does not attack glass, and boils at -40° . M. A. W.

Preparation of Crystalline Silicon and Boron. KARL AUGUST KÜHNE (D.R.-P. 147871).—Powdered oxides or hydroxides of silicon

or boron are mixed with aluminium turnings and sulphur and ignited. Thus 400 grams of aluminium, 500 grams of sulphur, and 360 grams of quartz may be mixed and covered with a thin layer of mixed powdered aluminium and sulphur, and ignited by means of a heated iron rod. The mass rapidly fuses, and reaches a white heat. When cold, the aluminium sulphide is decomposed by water, and the silicon remains in the crystalline form. Boron may be prepared from boric acid in similar manner. No external heat is required. C. H. D.

Solubility of Silicon in Zinc and Lead. HENRI MOISSAN and F. SIEMENS (*Compt. rend.*, 1904, 138, 657—661).—The metals were heated with excess of silicon in an electric resistance furnace at a constant temperature for about three hours. A pyrometer served to indicate the exact temperature. The following numbers were obtained :

| Lead. | | Zinc. | |
|--------------|---------------------------------|--------------|---------------------------------|
| Temperature. | Silicon dissolved in 100 grams. | Temperature. | Silicon dissolved in 100 grams. |
| 1250° | 0·024 grams. | 600° | 0·06 grams. |
| 1330 | 0·070 " | 650 | 0·15 " |
| 1400 | 0·150 " | 730 | 0·57 " |
| 1450 | 0·210 " | 800 | 0·92 " |
| 1500 | 0·780 " | 850 | 1·62 " |
| | | | S. S. |

Optical Properties of Vitreous Silica. J. W. GIFFORD and WILLIAM A. SHENSTONE (*Proc. Roy. Soc.*, 1904, 73, 201—208).—Vitreous silica possesses many properties which render it very valuable for optical work. It is indifferent to most corrosive fumes, it is transparent to ultra-violet radiations, and is not doubly refracting, whilst it is possible to produce two or more identical meltings. The refractive index is low. Measurements were made with prisms manufactured in different ways, one being built up from four separate meltings; the latter, however, was almost indistinguishable from the simple prism. Some of the indices of refraction obtained are given in the following table :

| | Wave length. | Index. | Wave length. | Index. |
|-----|--------------|-----------|--------------|----------|
| | 7950 | 1·453398 | 3034·21 | 1·486881 |
| (C) | 6563·04 | 1·4564147 | 2445·86 | 1·51096 |
| (D) | 5893·17 | 1·4584772 | 2062·0 | 1·54271 |
| (F) | 4861·49 | 1·463165 | 1852·2 | 1·5743 |

The dispersion is slightly greater than that of quartz. A thin doublet of fluorite achromatised by vitreous silica was examined and found to possess a focal length almost independent of wave length. Thus with a focal length of 1·00000, at wave lengths 7950 and 1852, the greatest variations reached 1·00086 for the *D* line and 0·99054 for wave length 2446. The indices of refraction in the table are probably in almost all cases correct to 1 in the 5th decimal place.

L. M. J.

Preparation of Sodium Oxide. BASLER CHEMISCHE FABRIK (D.R.-P. 148784. Compare Abstr., 1903, ii, 646, 724).—In the preparation of sodium oxide by heating sodium peroxide with metallic sodium, the reaction is greatly facilitated by the addition of a small proportion of sodium hydroxide. A much lower temperature is then required, and, the reaction being very rapid, the vessels employed are less corroded, and a purer product is obtained. The influence of the hydroxide is similar to that of moisture on the reaction between sodium and chlorine.
C. H. D.

Action of Carbon Dioxide on Solutions of Sodium Nitrite. CHARLES MARIE and R. MARQUIS (*Compt. rend.*, 1904, 138, 694—696. Compare this vol., i, 208; ii, 252).—An aqueous solution of β -naphthylamine and sulphanilic acid gives an orange-red colour with even traces of nitrous acid. With the aid of this reagent it is proved that carbon dioxide liberates small amounts of nitrous acid from solutions of sodium nitrite.
S. S.

Action of Carbon Dioxide on the Metallo-ammoniums. ETIENNE RENGADÉ (*Compt. rend.*, 1904, 138, 629—631).—At a temperature between -60° and -50° , carbon dioxide reacts with sodium ammonium to form sodium carbamate and hydrogen; the reaction is quantitative and represented by the equation $2\text{CO}_2 + 2\text{NH}_3\text{Na} = 2\text{NH}_2\cdot\text{CO}_2\text{Na} + \text{H}_2$. At a slightly higher temperature, -35° to -25° , the volume of hydrogen liberated is much less than that required by the above equation, and the product consists of a mixture of sodium carbamate and sodium formate, the latter being formed by the action of the nascent hydrogen on carbon dioxide in the presence of sodium ammonium (compare Moissan, Abstr., 1902, i, 255). Similar results were obtained with potassium-ammonium, but as this compound is more stable than the corresponding sodium compound (compare Moissan, Abstr., 1899, ii, 152) the operation could be conducted at a higher temperature, -10° to -5° , and a better yield of the formate was thus obtained.
M. A. W.

A New Mode of Formation of Calcium Carbide. HENRI MOISSAN (*Compt. rend.*, 1904, 138, 661—663).—When carbon electrodes are used in the electrolysis of fused calcium chloride, a certain amount of calcium carbide is formed by the union of calcium with the electrodes. The presence of the carbide can be recognised by the formation of acetylene on treating the product of electrolysis with water; the gaseous mixture obtained contains from 11.5—14.6 per cent. of acetylene. The yield of carbide can be improved by adding calcium fluoride and petroleum coke to the electrolytic bath. With these precautions, a product can be obtained which yields a gas containing as much as 65.7 per cent. of acetylene.
S. S.

Fluorides, Fluorochlorides, Fluorobromides, and Fluoroiodides of the Alkaline Earth Metals. EDOUARD DEFACQZ (*Ann. Chim. Phys.*, 1904, [viii], 1, 337—362).—A detailed account of the preparation, properties, and method of analysis of the fluorides and

double fluorides of calcium, barium, and strontium. The fluoride of calcium and the double fluorides of barium have been already described (compare this vol., ii, 123, 170).

Barium fluoride has not been obtained in a crystalline form owing to its insolubility in manganese chloride, bromide, or iodide.

Strontium fluoride is obtained in the form of octahedral crystals by fusing a mixture of manganese fluoride and strontium iodide.

Calcium and strontium fluorochlorides closely resemble the corresponding barium compound, but they are more readily dissociated by water; they form colourless, transparent crystals; the sp. gr. of the strontium compound is 4.18, that of the calcium 3.07.

Calcium fluorobromide, $\text{CaF}_2\text{CaBr}_2$, sp. gr. 3.15, and *strontium fluorobromide*, $\text{SrF}_2\text{SrBr}_2$, sp. gr. 4.06, are crystalline compounds, more readily decomposed by water than the barium compound.

Calcium fluoroiodide, CaF_2CaI_2 , has not been obtained pure owing to its deliquescent nature. *Strontium fluoroiodide*, SrF_2SrI_2 , has a sp. gr. 4.5 at 18°.

M. A. W.

Decomposition of Carbonates of the Alkaline Earths by Ammonium Chloride in presence of Water. H. CANTONI and G. GOGUELIA (*Bull. Soc. chim.*, 1904, [iii], 31, 282—287).—When powdered barium carbonate is added to an aqueous solution of ammonium chloride, it is decomposed with the formation of barium chloride and the liberation of ammonia and carbon dioxide. When the mixture is boiled, the reaction proceeds rapidly: thus, a solution containing 197.4 grams of ammonium chloride in 500 c.c. decomposed 9.87 grams of barium carbonate immediately, whilst solutions containing respectively 53.5 and 21.4 grams of ammonium chloride in 500 c.c. decomposed 9.87 grams of barium carbonate in 45 minutes and 16 hours respectively.

At the atmospheric temperature, 5.35, 10, and 20 per cent. solutions of ammonium chloride decomposed respectively 0.919325, 1.255651, and 1.5 grams of barium carbonate in 98 days.

Calcium carbonate is decomposed more slowly by ammonium chloride than is barium carbonate, and the strontium salt more slowly than calcium carbonate. A tabular statement showing the rates at which these salts are decomposed is given in the original. It is suggested that other salts of the alkaline earth metals may be decomposed by ammonium chloride in similar manner.

These results indicate the necessity of avoiding the addition of salts of the alkaline earths in the determination of alkali metals in silicates.

T. A. H.

Electrochemical Behaviour of Radium. ALFRED COEHN (*Ber.*, 1904, 37, 811—816).—Radium cannot be deposited on a platinum electrode by electrolysis of solutions in alcohol, acetone, or pyridine, as the cathode shows only a temporary induced activity.

With aqueous solutions, cathodes of different metals acquire only a temporary activity in presence of radium bromide solutions; a mercury cathode, however, becomes permanently active, and when extracted with hydrogen bromide gives a permanently active bromide.

The D.P. required for the separation of metal (calculated from heats of formation) increases in the series Ca, Sr, Ba, but proceeds in the reverse direction when amalgams are produced, so that the separation of strontium on mercury requires 0.2 volt more than barium, and calcium 0.25 volt more than strontium; the latter difference is sufficient for the electrolytic separation of these metals.

These values are, however, for saturated solutions, and although the difference between radium and barium should be greater than between barium and strontium, it is not possible to separate these metals except with extraordinarily small current densities; metallic radium is, however, precipitated by barium amalgam. Neither barium nor radium can be separated from aqueous solution on fused Wood's metal.

Metallic radium cannot be satisfactorily deposited on amalgamated platinum, but can be obtained on amalgamated zinc, the upper part of the rod being protected from oxidation by means of paraffin wax.

By precipitation on a pure mercury cathode and dissolution in hydrogen bromide, a considerable increase of activity is obtained in the bromide.

A silver anode was used to absorb the bromine; this at first showed a greater activity than the cathode, but this was due only to induced activity, and disappeared at the end of 24 hours.

The redissolving of the metallic radium in the solution from which it is being deposited can be greatly checked by using methyl alcohol as the solvent in place of water.

Metallic radium in the form of amalgam behaves like its compounds in that the activity increases during several days to a maximum value.

T. M. L.

Atomicity and Atomic Weight of Glucinum. SEBASTIAN M. TANATAR (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 82—86).—In this preliminary communication, the author gives it as his opinion that glucinum is a quadrivalent element of atomic weight 18.2, and that the compounds described by Urbain and Lacombe (*Abstr.*, 1902, i, 132 and 418) as of the type $\text{Be}_4\text{O}(\text{OR})_6$ have the formula Be_2OR_6 and the constitution $\text{R}_3\text{:Be}\cdot\text{O}\cdot\text{Be}:\text{R}_3$, for example, $\text{Be}(\text{OAc})_3\cdot\text{O}\cdot\text{Be}(\text{OAc})_3$. The atomic weight 18.2 multiplied by the specific heat at low temperatures (0.3756—0.409) gives 6.8—7.4 for the atomic heat. Attempts to prepare alums containing glucinum and rubidium or caesium yielded readily soluble double salts which possess neither the composition nor the crystalline form of alums but crystallise in the rhombic and monoclinic systems.

T. H. P.

Magnesium Potassium Carbonate. FRIEDRICH AUERBACH (*Zeit. Elektrochem.*, 1904, 10, 161—169).—The solubility of trihydrated magnesium carbonate, $\text{MgCO}_3\cdot 3\text{H}_2\text{O}$, in solutions of potassium hydrogen carbonate of various concentrations, up to about 1.1 normal, is determined at 15°, 25°, and 35°. The experiments were arranged so as to prevent loss of carbon dioxide from the solutions. At any one temperature, the solubility of the magnesium carbonate increases as the concentration of the potassium hydrogen carbonate increases, until the

point is reached at which the double salt, $\text{MgCO}_3 \cdot \text{KHCO}_3 \cdot 4\text{H}_2\text{O}$, begins to be formed; thereafter, the concentration of magnesium carbonate in the saturated solution diminishes. The solubility of magnesium carbonate diminishes as the temperature rises, whilst the solubility product of the double salt increases. From this, it follows that the formation of the double salt from $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ and potassium hydrogen carbonate solution is accompanied by a development of heat, and that the minimum concentration of potassium hydrogen carbonate required for its formation is smaller at lower temperatures than at higher ones. The whole series of conditions under which the existence of the double salt is possible are included in the interval of transition, the upper and lower limits of which are not practically realisable owing to the formation of $\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$ at low temperatures, and of the double salt, $\text{K}_2\text{CO}_3 \cdot \text{MgCO}_3 \cdot 4\text{H}_2\text{O}$, at higher ones. T. E.

Lead Tin Alloys. I. Chemical Equilibrium of Lead and Tin in presence of Solutions of their Salts. OTTO SACKUR (*Chem. Centr.*, 1904, i, 863—864; from *Arb. Kais. Ges.-A.*, 20, 512—544).—Lead is almost completely precipitated from its solution in acetic acid by tin, whilst, on the other hand, tin is precipitated from its solution in nitric acid by lead. In the case of solutions in hydrochloric acid or sulphuric acid, a state of equilibrium between the lead and tin and the salts of these metals is established. The conditions of equilibrium have been determined with varying amounts of free acid, and the results found to agree with a formula deduced from Nernst's theory, and the law of mass action. The behaviour of the metals towards different acids is explained on the assumption that lead has a greater solution tension than tin, and that the stannous salts, with the exception of the nitrate, are only very slightly dissociated into ions. Measurements of the *E.M.F.* of a voltaic element of the form $\text{Pb} \mid \text{Pb}(\text{NO}_3)_2 \mid \text{Sn}(\text{NO}_3)_2 \mid \text{Sn}$ showed that the electrolytic solution tension of lead is about 17.2 times as great as that of tin.

The lead was determined by adding ammonium sulphide to the solution containing lead and tin, dissolving the lead sulphide in a 15 per cent. solution of nitric acid, and precipitating the lead electrolytically. The filtrate from the lead sulphide was treated with sulphuric acid, the sulphide of tin collected, washed with ammonium sulphide, and weighed as dioxide. The electrolytic separation of tin from its solution in ammonium sulphide by Neumann's method was found to be inaccurate, the precipitated metal always containing sulphur. The volumetric estimation of pure stannous salts in acid solution by oxidation with ferric salts and titration with permanganate, or by adding excess of iodine solution and titrating with thiosulphate, gives concordant results only when a considerable excess of the oxidising agent is used. The presence of lead causes errors in the permanganate method, but lead salts do not affect the iodine method; in the latter, sodium or potassium acetate should be used to dissolve iodide of lead, and not ammonium acetate. E. W. W. Δ

Lead Carbonate. ROBERTO SALVADORI (*Gazzetta*, 1904, 34, i, 87—92).—Ammonium carbonate precipitates from a cold solution of

lead nitrate the normal carbonate, PbCO_3 , but when this is boiled with water for some time, carbon dioxide is evolved and the basic carbonate, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, formed. The same product is obtained on boiling the normal carbonate with $N/100$, $N/20$, and $N/10$ aqueous solutions of sodium sulphate or sodium chloride, and on boiling lead chloride or lead sulphate with an equivalent quantity of aqueous sodium carbonate. On adding to a mixture of lead sulphate and carbonate a solution containing sodium sulphate and carbonate, the whole of the sodium carbonate is converted into sodium sulphate when the latter is present in large excess, lead carbonate being formed. Similarly, when lead nitrate is added to a solution containing both sodium sulphate and carbonate, lead carbonate only is precipitated, contrary to Findlay's theory of fractional precipitation (Abstr., 1900, ii, 716); the whole of the sodium carbonate is precipitated before any lead sulphate is formed.

W. A. D.

Halogen Compounds of Mercury. MILES S. SHERRILL (*Zeit. physikal. Chem.*, 1904, 47, 103—106. Compare Abstr., 1903, ii, 534, 649).—When allowance is made for the dissociation $\text{HgX}_2 \rightleftharpoons \text{HgX}^+ + \text{X}'$, where $\text{X} = \text{Cl}, \text{Br}$, or I , the calculations made in the author's previous papers must be somewhat modified.

J. C. P.

Hydrolysis of Mercuric Chloride. ROBERT LUTHER (*Zeit. physikal. Chem.*, 1904, 47, 107—112. Compare Morse, Abstr., 1903, ii, 12; Sherrill, Abstr., 1903, ii, 534, 649; preceding abstract).—According to Ley (Abstr., 1900, ii, 67), the conductivity of a mercuric chloride solution is due to the hydrochloric acid formed by hydrolysis, but the author shows that in solutions of medium concentration this is not entirely the case. The variation of the conductivity of mercuric chloride solutions with dilution is well represented by the formula $\chi v^{2/5} = \text{const.}$, as is shown by comparison with the actual measurements of Ley (*loc. cit.*) and Kahlenberg (Abstr., 1901, ii, 540). When Morse's results also are taken into account, it is probable that the hydrolysis of mercuric chloride in aqueous solution takes place according to the equation: $2\text{HgCl}_2 + \text{H}_2\text{O} = (\text{HgCl})_2\text{O} + 2\text{H}^+$. The concentrations (in mols. per litre) of the various components of a saturated aqueous solution of mercuric chloride at 25° are estimated as follows:

$\text{HgCl}_2, 2.6 \times 10^{-1}$; $\text{H}^+, 3.3 \times 10^{-4}$; $(\text{HgCl})_2\text{O}, 1.7 \times 10^{-4}$; $\text{Cl}', 4.8 \times 10^{-4}$; $\text{HgCl}', 1.5 \times 10^{-4}$; $\text{Hg}'', 1 \times 10^{-8}$; $\text{HgCl}_4'', 5 \times 10^{-6}$.

J. C. P.

Action of Copper on Chloric Acid with and without Electrolysis. ANDRÉ BROCHET (*Bull. Soc. chim.*, 1904, [iii], 31, 287—290. Compare Abstr., 1903, ii, 210 and 352; and this vol., ii, 249).—Copper is violently attacked by a concentrated solution (280 grams per litre) of chloric acid at 60 — 80° , and is rapidly dissolved even at the ordinary temperature, but is only slowly dissolved by the normal acid (83.5 grams per litre). In no case is any hydrogen evolved.

When a normal solution of chloric acid is electrolysed in the cold, using a copper anode, the latter is attacked regularly over its whole surface and becomes coated with a layer of cuprous chloride which,

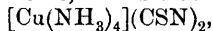
however, disappears on warming. Similarly, when copper is dissolved in a cold normal solution of chloric acid, the metal becomes covered with a layer of hydrated cuprous oxide. It appears, therefore, that the metal passes into solution in the cuprous form, the cuprous compound first produced being dissolved, if there is an excess of chloric acid present, forming cupric chloride and chlorate. With the concentrated acid, the reaction is complicated by the formation of oxygenated compounds of chlorine, and in the absence of an excess of free chloric acid, complex basic salts are precipitated. T. A. H.

Formation of Basic Copper Salts under the Influence of Electrolysis. ANDRÉ BROCHET (*Bull. Soc. chim.*, 1904, [iii], 31, 290—293. Compare preceding abstract).—When metallic copper is placed in a solution of copper chlorate, the metal becomes coated with a layer of hydrated cuprous oxide and cupric chloride appears in the solution. Ultimately a pale blue precipitate having the composition represented by the general formula $\text{Cu}(\text{X})_2 \cdot 3\text{Cu}(\text{OH})_2$ is produced, in which X is a mixture of the radicles Cl and ClO_3 , the former predominating. It is suggested that this precipitate is formed by the oxidation, at the expense of the copper chlorate, of the cuprous oxide to cupric oxide, which then combines with the cupric chloride and chlorate in the solution.

When a solution of copper chlorate is electrolysed (compare this vol., ii, 249), using a copper anode, the latter is attacked irregularly and is eventually converted into a lace-like mass of filaments; the negative pole becomes coated with a non-coherent layer of copper containing some chloride, and there is formed a pale blue precipitate of a complex basic salt, conforming to the general formula already given, but in which X is principally represented by the radicle ClO_3 . It is suggested that this compound is formed in the manner already indicated, and that this reaction affords an explanation of the observed fact that the ratio between the amount of copper dissolved and that deposited in the voltameter under these conditions varies from 1.5 to 2 according to the conditions of the experiment. T. A. H.

Basic Cupric Chlorate. ANDRÉ BROCHET (*Bull. Soc. chim.*, 1904, [iii], 31, 293).—The basic cupric chlorate, $\text{Cu}(\text{ClO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$, described by Bourgeois (*Abstr.*, 1899, ii, 157), has been obtained in a slightly impure amorphous form by adding to cold aqueous solutions of cupric chlorate, cupric hydroxide or hydroxides of the alkalis or alkaline earths. The product obtained invariably contained an excess of cupric hydroxide and a quantity of water, which was not lost by exposure under reduced pressure or by heating at 100° . T. A. H.

Complex Copper Compounds. VOLKMAR KOHLSCHÜTTER (*Ber.*, 1904, 37, 1153—1171. Compare *Abstr.*, 1903, i, 468).—[With P. PUDSCHIES].—When any cupric salt is dissolved in concentrated ammonia and rather more than an equivalent quantity of potassium thiocyanate is added, dark blue, rhombic tablets of the salt,



separate. This dissolves in water to a violet solution, from which

potassium thiocyanate precipitates bright blue, insoluble needles of the compound $[\text{Cu}(\text{NH}_3)_2](\text{CSN})_2$. Other alkali salts do not produce this precipitate, but it is obtained whenever the concentration of ammonia in the solution is diminished by dilution, warming, or exposure to air. On adding potassium iodide to a solution of cuprammonium iodide, $[\text{Cu}(\text{NH}_3)_4]\text{I}_2 \cdot \text{H}_2\text{O}$, the colour changes gradually from violet to green, and large, almost black crystals of the compound $\text{Cu}_3(\text{NH}_3)_{10}\text{I}_6$ separate. This is probably identical with a salt obtained by Richards and Oenslager (Abstr., 1895, i, 330), and is to be regarded as a double compound, $2[\text{CuI}(\text{NH}_3)_3]\text{I} \cdot [\text{Cu}(\text{NH}_3)_4]\text{I}_2$. Potassium oxalate precipitates blue crystals of the salt $\text{Cu}(\text{NH}_3)_4\text{I}_2(\text{C}_2\text{O}_4) \cdot 6\text{H}_2\text{O}$.

Cuprammonium oxalate, $\text{Cu}(\text{NH}_3)_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, is precipitated in the form of vitreous, blue prisms, often forming crossed twins, from a solution of cuprammonium sulphate, $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$, by potassium oxalate, even in presence of a considerable excess of ammonia.

Cuprammonium bromide, $\text{Cu}_3(\text{NH}_3)_{10}\text{Br}_6$, is only obtained on warming. Potassium bromide precipitates bluish-green crystals of a basic salt, $\text{Cu}(\text{NH}_3)_2\text{Br}_2 \cdot 2\text{CuO} \cdot 3\text{H}_2\text{O}$, from its solution.

Experiments on the electrolytic transport of aqueous solutions of cupric chloride lead to the conclusion that the cathion in such solutions is a complex containing water molecules, and that the equilibrium, $[\text{CuCl}(\text{H}_2\text{O})_3]^+ + \text{H}_2\text{O} \rightleftharpoons [\text{Cu}(\text{H}_2\text{O})_4]^+ + \text{Cl}^-$, is displaced by a rise of temperature in the direction of the lower arrow. A few experiments with solutions of cupric chloride in acetone are also described.

C. H. D.

Absorption of Oxygen by Alkaline Cerous Solutions. EMIL BAUR (*Ber.*, 1904, 37, 795—798).—The absorption of oxygen by alkaline cerous solutions is greatly influenced by the degree of alkalinity and by the character of the cerium salt. Three specimens, *A* nitrate, *B* and *C* chloride, gave the following absorptions in percentages of peroxide salt formed: *A*, 55, 48, 56, 54.2, 55; *B*, 52.3, 44.2, 37.2, 51.2, 52.3, 55, 44, 52.3; *C*, 72.1, 62.1, 72.0. Specimen *B*, which gave about 50 per cent. absorption in presence of potassium carbonate, gave 60.1, 75.9, 67.8, 59.3, 76.3 and 62.8 per cent. when the carbonate was partially converted into hydrogen carbonate, whilst when sodium hydroxide was added to the carbonate the absorption of oxygen was scarcely greater than that required to convert the cerous into a ceric salt.

T. M. L.

Adsorption Compound formed by Iodine with Basic Lanthanum Acetate. WILHELM BILTZ (*Ber.*, 1904, 37, 719—724).—The author has determined the amount of iodine removed from its solution in potassium iodide by known quantities of the gelatinous precipitate formed by adding ammonia to a solution of lanthanum acetate. It varies largely according to the physical state of the precipitate, the amount of iodine absorbed being greatest in the case of the flocculent, semi-transparent colloidal mass obtained by Damour's method (*Compt. rend.*, 1857, 43, 976), a deep blue colour being produced; when the precipitate is formed in boiling solution, it is granular and absorbs little iodine, a brownish-black colour being

the result. Approximately the same proportion of the total amount of iodine is removed by a fixed quantity of the same precipitate from solutions containing varying amounts of iodine. Thus, with solutions containing from 1.88—0.105 grams of iodine, the ratio of iodine remaining unabsorbed to iodine absorbed varied only from 7.2—8.3. Another preparation gave values varying from 9—12 for the same ratio. These results are similar to those obtained by Küster (Abstr., 1895, i, 199) in the case of iodine and starch; it may be concluded that the blue colour produced by iodine with lanthanum acetate does not correspond with the formation of a definite compound. The analogy with starch is made complete by the fact that a colloidal solution of basic lanthanum acetate, prepared by dialysis, absorbs iodine according to the same law. W. A. D.

Europium. GEORGES URBAIN and HENRI LACOMBE (*Compt. rend.*, 1904, 138, 627—629).—From 610 grams of the mixed oxides of samarium, europium, and gadolinium obtained from 500 kilos. of monazite sand, the authors have separated, by a method already described (compare this vol., ii, 37, 173), six fractions consisting of the pure europium salt, representing 2 parts of europium oxide in 100,000 parts of the mineral. No differences could be detected in any of these fractions, so that if europium is a mixture, its components cannot be separated by fractionation of the double magnesium salts. *Europium sulphate*, $\text{Eu}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, is obtained in well-formed crystals having a rose colour, is unaltered in air, is dehydrated at 375° , and converted into the oxide at 1600° ; the oxide thus obtained has a rose colour, whilst that prepared at a lower temperature by calcining the oxalate is white with a faint rose tint in mass.

The atomic weight of europium, as determined (1) by the conversion of the hydrated sulphate into the anhydrous salt, (2) by the conversion of the anhydrous sulphate into the oxide, (3) by the conversion of the hydrated sulphate into the oxide (5 determinations in each case), is 151.79, with an error of not more than 0.06 (compare Demarcay, Abstr., 1900, ii, 481; 1901, ii, 511). M. A. W.

General Method of Preparing Anhydrous Chlorides. CAMILLE MATIGNON and F. BOURION (*Compt. rend.*, 1904, 138, 631—633. Compare Abstr., 1901, ii, 602; 1902, ii, 263, 505).—A mixture of chlorine and sulphur chloride (S_2Cl_2) is a convenient agent for preparing the anhydrous metallic chlorides from the corresponding oxide, in that it possesses both chlorinating and reducing properties and reacts at a comparatively low temperature. By passing a stream of chlorine saturated with sulphur chloride over the heated oxide, the following compounds were obtained: (1) silicon tetrachloride, SiCl_4 , boiling at 59° , from silica heated to a dull redness. (2) A double chloride of aluminium and sulphur, $\text{Al}_2\text{Cl}_6 \cdot \text{S}_2\text{Cl}_2$, a yellow oil which solidifies on cooling; prepared from alumina heated at 350° to 400° . (3) Thorium tetrachloride, ThCl_4 , beautiful, prismatic needles 1—2 cm. long; prepared from thoria heated to low redness. (4) The chlorides of praseodymium, neodymium, and samarium, from the corresponding oxides or carbonates; in this case, the heating has to be gradual to avoid fusing

the mixture of chloride and oxychloride first formed. (5) Vanadium tetrachloride, VCl_4 , boiling at 150° with partial decomposition into chlorine, and the sesquichloride, V_2Cl_6 . The chlorinating mixture attacks vanadium oxide in the cold, with the formation of the oxychloride, VOCl_3 , boiling at 126° . This is, however, converted into the tetrachloride by mixing with excess of sulphur chloride and heating to dull redness.

M. A. W.

Transformation of Oxides and Oxygenated Salts into Chlorides. CAMILLE MATIGNON and F. BOURION (*Compt. rend.*, 1904, 138, 760—762. Compare preceding abstract).—By means of a mixture of chlorine and sulphur chloride, oxides and oxygenated salts are converted into anhydrous chlorides; the reaction in some cases proceeds quantitatively and is suitable for analytical purposes. Tungsten trioxide, when strongly heated with the chlorinating mixture, gives the oxychloride, WO_2Cl_2 , in brilliant, yellow plates subliming at 264° without previous fusion; at a lower temperature, the oxychloride, WOCl_4 , is formed in slender, red needles which melt at 211° [compare, however, Smith and Flack, *Abstr.*, 1900, ii, 81]. Chromium sesquioxide and ferric oxide are rapidly and completely converted into the corresponding anhydrous chlorides when heated below redness in a mixture of chlorine and sulphur chloride; nickel and cobalt oxides are similarly chlorinated at 400° , the reaction being accompanied by incandescence; zinc, manganese, and tin oxides are also converted into the corresponding anhydrous chlorides when heated below fusion in the chlorinating mixture. Boron trioxide has not been converted into the chloride by the action of chlorine and sulphur chloride. Barium and calcium sulphates and barium carbonate are converted quantitatively into their respective chlorides when heated with the chlorinating mixture, and the method has been applied to the analysis of mixtures of iron oxide and barium sulphate, and chromium sesquioxide and barium sulphate, the resulting mixed chlorides being separated by sublimation in the first case and by solution in the second.

M. A. W.

Electrolytic Preparation of Aluminium. GUSTAVE GIN (D.R.-P. 148627).—A mixture of sodium aluminium fluoride and sodium thioaluminate, prepared by fusing together aluminium fluoride and sodium sulphide: $2\text{Al}_2\text{F}_6 + 6\text{Na}_2\text{S} = \text{Al}_2\text{F}_6, 6\text{NaF} + \text{Al}_2\text{S}_3, 3\text{Na}_2\text{S}$, may be electrolysed in the fused state. The thioaluminate is decomposed by the current: $\text{Al}_2\text{S}_3, 3\text{Na}_2\text{S} = 3\text{Na}_2\text{S} + 2\text{Al} + 3\text{S}$, and the sodium sulphide then reacts with the double fluoride: $\text{Al}_2\text{F}_6, 6\text{NaF} + 3\text{Na}_2\text{S} = 12\text{NaF} + 2\text{Al} + 3\text{S}$. Bauxite is used, and is dissolved in hydrofluoric acid; precipitated alumina or bauxite is then added to remove iron, silicon, and titanium. The process is cyclic, the sulphur produced being burnt to sulphuric acid, which is then used to prepare the hydrofluoric acid from the sodium fluoride formed in the electrolysis. The sodium sulphate thus produced is heated with coal to regenerate sodium sulphide.

C. H. D.

Estimation of Sulphuric Acid. RICHARD SILBERBERGER (*Monatsh.*, 1904, 25, 220—248. Compare Abstr., 1903, ii, 751).—The estimation of sulphuric acid by precipitation as barium sulphate is known to give inaccurate results in presence of iron, chromium, aluminium, or potassium salts. The object of the investigation was to determine the nature of the compounds retained by the barium sulphate.

Aluminosulphuric acid, $\text{Al}_2(\text{SO}_4\text{H})_6 \cdot 7\text{H}_2\text{O}$, is prepared by adding aluminium sulphate to cold concentrated sulphuric acid and warming, when a voluminous white precipitate separates. On diluting with ether, filtering, and washing with ether, the acid is obtained as a white powder, decomposing in moist air and dissolving in water, the solution soon decomposing into aluminium sulphate and sulphuric acid.

No definite product could be obtained from chromic sulphate or ferric sulphate and sulphuric acid in similar manner, although several chromosulphuric acids have been isolated by Recoura (Abstr., 1893, ii, 470). The addition of barium chloride to solutions of aluminium or chromic sulphate in concentrated sulphuric acid also yielded products to which no formula could be assigned; they contain barium sulphate arising from the decomposition of the complex salt originally formed.

The barium ferrisulphate described by Küster and Thiel (Abstr., 1900, ii, 242) is probably $\text{Ba}_3\text{Fe}_2(\text{SO}_4)_6$, from its decomposition into barium sulphate, ferric oxide, and sulphur trioxide on ignition (Jannasch and Richards, Abstr., 1889, 926).

On adding barium nitrate to a concentrated solution of potassium sulphate and potassium nitrate, a white, unstable salt is precipitated, which, after drying over sulphuric acid, has the composition $\text{NO}_3 \cdot \text{Ba} \cdot \text{SO}_4 \cdot \text{Ba} \cdot \text{SO}_4 \cdot \text{K}$. Boiling dilute hydrochloric acid only removes a portion of the alkali. The salt obtained from barium chloride, potassium sulphate, and potassium chloride has the composition $\text{Cl} \cdot \text{Ba} \cdot \text{SO}_4 \cdot \text{Ba} \cdot \text{SO}_4 \cdot \text{Ba} \cdot \text{SO}_4 \cdot \text{K}$. Sodium salts are not retained by barium sulphate in the form of complex salts. Platinum salts are also not retained.

The remainder of the paper contains an account of the author's method of precipitation of sulphates with strontium chloride in alcoholic solution (*loc. cit.*). C. H. D.

Atomic Weight of Indium. LOUIS M. DENNIS and WILLIAM C. GEER (*Ber.*, 1904, 37, 961—962. Compare Thiel, this vol., ii, 177).—An alcoholic solution of anhydrous indium chloride gives a heavy, colourless precipitate with pyridine, which only redissolves in a large excess of pyridine; indium chloride can in this manner be completely separated from iron and aluminium chlorides. A method based on this is being used to purify indium for atomic weight determinations. Metallic indium can be deposited electrolytically from solutions of its chloride or nitrate in either pyridine, hydroxylamine, or formic acid.

Indium nitrate forms a double salt with ammonium nitrate, which crystallises in large, colourless prisms. E. F. A.

Preparation of Metallic Silicides; Manganese Silicides. PAUL LEBEAU (*Ann. Chim. Phys.*, 1904, [viii], 1, 553—574).—A detailed account of the preparation and properties of the manganese silicides, SiMn_2 , SiMn , and Si_2Mn (compare Abstr., 1903, ii, 215, 298, 652). The silicide, SiMn_2 , has the sp. gr. 6.40 at 15° , and not 6.20 as stated in the earlier paper. M. A. W.

Formation of Magnetite by Heating Iron in Carbon Dioxide. JULIUS DONAU (*Monatsh.*, 1904, 25, 181—187. Compare Baur and Glaessner, Abstr., 1903, ii, 423).—According to Tissandier (this Journal, 1872, 284), iron is converted into ferrous oxide by heating at 900° in a current of dry carbon dioxide.

Experiments in which pure iron wire was heated at 1200° in a current of dry carbon dioxide showed that the product is ferrosiferrous oxide, which resembles natural magnetite in appearance, crystalline form, density, hardness, &c. The product is magnetic, and the crystals often show magnetic polarity, especially when the heating has been carried out in an electric furnace. The presence of moisture in the carbon dioxide has no influence on the result, except that the formation of large crystals is facilitated. C. H. D.

Variable Hydrolytic Equilibrium of Dissolved Chromium Sulphate. THEODORE W. RICHARDS and FREDERIC BONNET (*Zeit. physikal. Chem.*, 1904, 47, 29—51).—When a violet solution of chromium sulphate is subjected to dialysis, examination of the salt that has diffused and of the salt that has remained in the dialyser shows that the ratio Cr/SO_4 is the same in both. When, however, a green solution of chromium is similarly treated, the ratio Cr/SO_4 diminishes in the diffused portion and increases in the dialyser—an observation in favour of the view that the change from violet to green involves a hydrolysis with formation of free acid and a soluble basic salt. The extent of the hydrolysis was estimated by comparing the influence of the green solution on the rate of inversion of sugar with that of a hydrochloric acid solution of known strength. The acid produced by hydrolysis at 100° in a $\frac{1}{4}$ -molar solution of chromium sulphate is about $0.13N$; that produced by hydrolysis at 50° is about $0.1N$. These values are, if anything, too low, since a green solution reverts slowly to the violet condition at the ordinary temperature. The violet solution itself inverts sugar very slowly, but if a violet solution and a green solution (both $\frac{1}{4}$ -molar) are kept for about a month at 30° , the amount of acid present (as indicated by the sugar inversion method) becomes the same in the two cases (about $0.043N$). Thus the hydrolytic equilibrium between the violet and the green salts varies with the temperature.

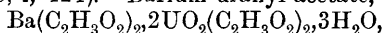
When the violet solution is boiled, cooled, and immediately extracted with a mixture of alcohol and ether, the acid is removed, and it is thus possible to get the ratio Cr/SO_4 in the residual green solution as high as 1/1. If the acid is removed by digesting at 100° with chromic hydroxide, the same final value of the ratio is obtained, but if the violet solution is saturated with the hydroxide at 20° , it becomes green, and the ratio Cr/SO_4 assumes finally the value $5/4$.

When barium sulphate is precipitated from a green solution of chromium sulphate, it carries down with it small quantities of a green, strongly basic chromium sulphate, the amount of this depending on the extent to which hydrolysis has taken place. If the precipitation takes place in a violet solution, scarcely any chromium is carried down with the barium sulphate (compare Richards, Abstr., 1900, ii, 472; Richards, McCaffrey, and Bisbee, Abstr., 1901, ii, 624).

Electrolytic experiments showed that there is no complex chromium anion in the green solutions of the sulphate.

The work detailed in the paper points to the existence of a green basic salt, in which at least 47 per cent. of the acid radicle is replaced by hydroxyl. It is not possible to give a definite formula to this basic salt, and there may exist several compounds hydrolysed to different degrees. J. C. P.

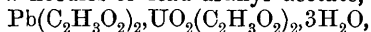
Barium and Lead Uranyl Acetates and the Corresponding Uranates. JOSEF ZEHENTER (*Monatsh.*, 1904, 25, 197—219. Compare Abstr., 1900, i, 424).—Barium uranyl acetate,



prepared by concentrating an acid solution of the mixed acetates in a vacuum, loses $3\text{H}_2\text{O}$ at 200° , and is decomposed, yielding barium diuranate, BaU_2O_7 , between 300° and a red heat. On boiling the acetate with water, a yellow, crystalline mass of *barium triuranate*, $\text{BaU}_3\text{O}_{10} \cdot 4\frac{1}{2}\text{H}_2\text{O}$, is obtained, which loses $2\frac{1}{2}\text{H}_2\text{O}$ at 140° , and the remaining $2\text{H}_2\text{O}$ at low redness. On heating a solution of the acetate on the water-bath and continually replacing the water evaporated, the whole of the uranium is precipitated in the form of *barium pentauranate*, $\text{Ba}_2\text{U}_5\text{O}_{17} \cdot 8\text{H}_2\text{O}$, which forms golden-yellow crystals; these lose $4\frac{1}{2}\text{H}_2\text{O}$ at 140° , and the remaining water of crystallisation at low redness. If the solution contains an excess of barium acetate, barium diuranate is precipitated. When a 1 per cent. solution of barium uranyl acetate is boiled for 4—5 hours in a reflux apparatus, yellow, microscopic, hexagonal leaflets of *barium heptauranate*, $\text{Ba}_2\text{U}_7\text{O}_{23} \cdot 11\text{H}_2\text{O}$, separate. This salt loses $2\frac{1}{2}\text{H}_2\text{O}$ at 110° , and the remaining $8\frac{1}{2}\text{H}_2\text{O}$ at low redness.

A solution of barium and uranyl acetates, kept in a closed flask in diffused daylight or in darkness, slowly deposits small, prismatic crystals of a *salt*, $\text{BaU}_3\text{C}_4\text{H}_{10}\text{O}_{15} \cdot 6\frac{1}{2}\text{H}_2\text{O}$, which loses $6\frac{1}{2}\text{H}_2\text{O}$ in a vacuum, and a further $2\text{H}_2\text{O}$ is evolved on heating to 250° . The compound is probably to be regarded as $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{UO}_3 \cdot 2\text{H}_2\text{O}$. Acetone is evolved on ignition, and barium triuranate remains.

Solutions of lead and uranyl acetates, evaporated in a vacuum, deposit silky, yellow needles of lead uranyl acetate,



becoming anhydrous in a vacuum-desiccator. Lead uranate, PbUO_4 , remains on ignition as a reddish-brown, crystalline mass. When a dilute solution of the double salt is boiled in a reflux apparatus, golden-yellow crystals of lead diuranate, $\text{PbU}_2\text{O}_7 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, separate, becoming anhydrous on ignition. A less dilute solution deposits a reddish-yellow precipitate of *lead enneuranate*, $\text{Pb}_5\text{U}_9\text{O}_{32} \cdot 10\text{H}_2\text{O}$, becoming anhydrous on ignition. Slow evaporation in an open dish on the water-bath causes the deposition of yellow crystals of *lead pentauranate*, $\text{Pb}_4\text{U}_5\text{O}_{19} \cdot 4\text{H}_2\text{O}$, becoming anhydrous on ignition. At

temperatures below 5° , prismatic crystals of the salt, $[\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2, 3\text{UO}_3, 2\text{H}_2\text{O}]3\text{H}_2\text{O}$, corresponding with the barium salt, are deposited. $3\text{H}_2\text{O}$ are evolved in a vacuum, and lead triuranate, $\text{PbU}_3\text{O}_{10}$, remains on ignition.

The results concerning water of crystallisation differ in some respects from those obtained by Wertheim (1843) and Rammelsberg (Abstr., 1885, 648). The types of salts obtained in the present and former paper (*loc. cit.*) are presented in tabular form. C. H. D.

Zirconium Tetraiodide, ZrI_4 . ARTHUR STÄHLER and BRUNO DENK (*Ber.*, 1904, 37, 1135—1139).—Zirconium tetraiodide has been described by Dennis and Spencer (Abstr., 1897, ii, 558) as a white, crystalline powder, not acted on by water or acids. The authors have re-investigated this compound, and obtain quite different results.

Zirconium tetraiodide is best prepared by heating metallic zirconium or the carbide, prepared by Moissan's method (Abstr., 1896, ii, 428), in a current of dry hydrogen iodide. A vigorous reaction sets in at 340° in the case of the metal, or at 490° in the case of the carbide, and a brown sublimate is formed. After removal of hydrogen iodide by hydrogen, the sublimate is digested with benzene at 100° in a sealed tube to remove free iodine. It is then filtered in an atmosphere of hydrogen, washed with benzene, and dried. The tetraiodide is a yellow, micro-crystalline powder, which fumes in air and dissolves in water or acids with a vigorous reaction. Alcohol also dissolves it, forming ethyl iodide and zirconic acid. Dry ether dissolves it to a yellow solution, first forming an additive product. Ammonia, propylamine, &c., also yield additive products with an ethereal solution of the tetraiodide, which will be further investigated.

For analysis, the iodide is dissolved under ether in water containing a little sulphurous acid. The zirconium is then precipitated by ammonia, and the iodine is determined in the filtrate as silver iodide.

A definite oxyiodide of zirconium has not yet been obtained (compare Venable and Baskerville, Abstr., 1898, ii, 596). By dissolving the tetraiodide in water, or by dissolving zirconium hydroxide in hydriodic acid, and evaporating, colourless, hygroscopic needles of the composition $\text{ZrOI}_2, 8\text{H}_2\text{O}$ are obtained, dissolving readily in water or alcohol. The composition corresponds with that of the known oxychloride and oxybromide. C. H. D.

So-called Explosive Antimony. ERNST COHEN and WILHELM E. RINGER (*Zeit. physikal. Chem.*, 1904, 47, 1—28).—Explosive antimony has been prepared by electrolysing solutions of antimony trichloride containing free hydrochloric acid, and the authors have studied the variation of its composition with current density, with temperature, and with the concentration of the trichloride solution. Explosive antimony contains some trichloride, and extraction experiments, in which the powdered explosive product was treated with a mixture of alcohol and ether, showed that the enclosed trichloride is not held mechanically. It may, however, be driven out by heat, and may then be dissolved in the alcohol-ether mixture, the process actually employed in the analysis of the explosive antimony. The percentage of antimony

trichloride in this substance is independent of the amount of hydrochloric acid in the electrolysed solution, but is slightly diminished by an increase of current density. As the concentration of the trichloride in the electrolysed solution increases from 3.1 to 85.7 per cent., the percentage of trichloride in the explosive product increases from 1.64 to 10.5 per cent. The curve obtained by plotting the one percentage of trichloride against the other is discontinuous about the point corresponding with 10 per cent. of trichloride in solution, and it is significant that the metallic product obtained from solutions containing less than 10 per cent. of trichloride is not explosive. As the temperature of the electrolysed solution is raised, the percentage of antimony trichloride in the metallic product diminishes. J. C. P.

Alloys of Copper and Antimony and the Phenomenon of Recalescence observed in them. A. A. BAIKOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 111—165).—The author has prepared melting point curves and tables of alloys of copper and antimony, and also their cooling curves. The latter show that these alloys exhibit the phenomenon of recalescence.

Copper and antimony form two compounds, SbCu_2 and SbCu_3 . The former has a bright violet colour, whilst the second is white with a perceptible green tint. All alloys containing less than 51 per cent. of copper (corresponding with SbCu_2) have also a violet colour, which becomes fainter as the proportion of copper diminishes. The characteristic yellow colour of copper is only found in the alloys containing more than 70 per cent. of copper. The violet alloy, SbCu_2 , melts and decomposes at 586° , and can be prepared by melting SbCu_3 and antimony together in such proportions that solidification begins at a temperature below 586° ; mixtures of the two metals, which commence to solidify at higher temperatures than 586° , deposit only the alloy SbCu_3 , which melts at 681° . These results are in accord with those given by a study of the other physical properties of these alloys, hardness, expansion, and *E.M.F.* in galvanic elements.

The alloy SbCu_3 exists in two modifications: (1) the α -form, stable at temperatures below 407° , and (2) the β -form, stable at higher temperatures. All mixtures of the two metals containing from 53.5 to 61 per cent. of copper, and consisting of mixed crystals of antimony and the compound SbCu_3 , undergo, on cooling, two distinct changes: (1) polymorphic transformation of the β -form of SbCu_3 into the α -modification, and (2) separation of SbCu_3 .

The micro-structure of the different alloys confirms the above conclusions. T. H. P.

Structure of Fluorovanadium Compounds. PETR G. MELIKOFF and PAUL KAZANEZKY (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 77—82).—On the basis of their previous researches (Abstr., 1902, ii, 27), and of an examination of the compounds of vanadium oxyfluoride with potassium and ammonium fluorides, $\text{VO}_2\text{F} \cdot 2\text{KF}$ and $\text{VO}_2\text{F} \cdot \text{NH}_4\text{F}$, the authors conclude that these compounds are potassium and ammonium salts of orthovanadic acid, in which one atom of oxygen is replaced by

two atoms of fluorine and a hydroxyl group also replaced by one atom of fluorine ; the compounds hence have the structures : $\text{VF}_3(\text{OK})_2$ and $\text{NH}_4\text{F} \cdot \text{F} \cdot \text{VF}_2(\text{ONH}_4)_2$.
T. H. P.

Mineralogical Chemistry.

Cryolithionite, a New Mineral. N. V. USSING (*Overs. K. Danske Videnskab. Selsk. Forhandl.*, 1904, 3—12).—The new mineral occurs as large, colourless, rhombic dodecahedra in the cryolite of Ivigtut, Greenland. There is a good cleavage parallel to the faces of the rhombic dodecahedron, $H. 2\frac{1}{2}$ —3; sp. gr. 2·77; refractive index 1·3395(Na). The crystals contain cryolite and liquid enclosures. Analysis by Chr. Christensen of pure material gives the formula $Li_3Na_3Al_2F_{12}$. The mineral dissolves in 1350 parts of water at 18°, and from this solution crystallises as cubes. It fuses at about 710°, and on cooling crystallises in rectangular, arborescent forms.

| Al. | Na. | Li. | F. | Loss on ignition. | Total. |
|-------|-------|------|-------|-------------------|--------|
| 14·46 | 18·83 | 5·35 | 60·79 | 0·36 | 99·79 |

Although the mineral has certain points in common with cryolite (Na_3AlF_6), it is crystallographically more closely related to the garnet ($Ca_3Si_3Al_2O_{12}$) and sodalite groups.

Cryolithionite contains the highest percentage of lithium of any mineral yet known.

L. J. S.

[Tellurium and Tellurite from Colorado; Cuprodescloizite from Arizona.] WILLIAM P. HEADDEN (*Proc. Colorado Sci. Soc.*, 1903, 7, 141—150).—Analysis of pure cleavage fragments of native tellurium from the Goodhope mine, Gunnison Co., Colorado, gave: Te, 99·45; Fe, 0·11; Se, 0·40 = 99·96. Several analyses are also given of impure material, from the same locality and from Boulder Co., consisting of native tellurium intermixed with various tellurides, pyrites, quartz, &c.; some of these are fine grained and without recognisable cleavage.

Tellurite (TeO_2) occurs at the Goodhope mine as a white coating on the native tellurium, and also as brownish-yellow, granular masses of small crystals, which are perhaps tetragonal; analysis of the latter gave:

| Te. | Bi_2O_3 . | Fe_2O_3 . | Insol. | O. | Total. |
|-------|-------------|-------------|--------|---------|--------|
| 78·68 | trace | 0·70 | 1·04 | [19·58] | 100·00 |

Chestnut-brown, fibrous cuprodescloizite ($R_3V_2O_8R[OH]_2$) from Nogales, Arizona, gave:

| V_2O_5 . | As_2O_5 . | PbO. | CuO. | ZnO. | Fe_2O_3 . | MnO. | H_2O . | Insol. | Total. |
|------------|-------------|--------|-------|-------|-------------|-------|----------|--------|--------|
| 19·014 | 3·842 | 52·954 | 8·506 | 12·45 | 0·20 | trace | 2·65 | 0·35 | 99·996 |

L. J. S.

Some Californian Minerals. WALDEMAR T. SCHALLER (*Amer. J. Sci.*, 1904, [iv], 17, 191—194).—*Halloysite*.—A pink clay occurring in large seams at the lepidolite mine near Pala, San Diego Co., is shown by analysis I to be halloysite ($\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9 \cdot \text{H}_2\text{O}$). Other pink clays from the United States have proved to be montmorillonite and cimolite.

| | SiO_2 . | Al_2O_3 . | Fe_2O_3 . | MnO . | CaO . | MgO . | Li_2O . |
|----|-------------------------|---------------------------|---------------------------|----------------------|------------------|----------------|-------------------------|
| I. | 43·62 | 35·55 | 0·21 | 0·26 | 1·02 | 0·19 | 0·23 |
| | | | H_2O | H_2O | | | |
| | Na_2O . | K_2O . | (107°). | (>107°). | TiO_2 . | Total. | |
| | 0·19 | 0·03 | 6·63 | 12·25 | Nil. | 100·18 | |

Amblygonite.—A large deposit of massive, white amblygonite occurs at the lepidolite mine near Pala; analysis II:

| | P_2O_5 . | Al_2O_3 . | Fe_2O_3 . | MnO . | MgO . | Li_2O . | Na_2O . | H_2O . | F. | TiO_2 . | Total (less O for F). |
|-----|--------------------------|---------------------------|---------------------------|----------------|----------------|-------------------------|-------------------------|------------------------|------|------------------|-----------------------|
| II. | 48·83 | 33·70 | 0·12 | 0·09 | 0·31 | 9·88 | 0·14 | 5·95 | 2·29 | Nil. | 100·35 |

Boothite.—A massive, pale blue copper sulphate, sp. gr. 1·944, from the copper mine near Campo Seco, Calaveras Co., gave results (III) proving it to be boothite ($\text{CuSO}_4 \cdot \text{H}_2\text{O} \cdot 6\text{H}_2\text{O}$). A redetermination of the sp. gr. of purer material from the original locality (Abstr., 1903, ii, 490) gave 1·935:

| | CuO . | FeO . | MgO . | SO_3 . | $\text{H}_2\text{O}(110^\circ)$. | $\text{H}_2\text{O}(>110^\circ)$. | Insol. | Total. |
|------|----------------|----------------|----------------|-----------------|-----------------------------------|------------------------------------|--------|--------|
| III. | 26·13 | 0·81 | 0·64 | 27·25 | 36·76 | 4·91 | 3·96 | 100·46 |
| IV. | 7·56 | 15·85 | — | 30·74 | 45·85 | [About 6 p.c. deducted.] | | 100·00 |

Pisanite.—Analysis of a massive specimen from Gonzales, Monterey Co., gave results (IV) agreeing approximately with the formula $\text{CuO} \cdot 2\text{FeO} \cdot 3\text{SO}_3 \cdot 21\text{H}_2\text{O}$. Previously published analyses of pisanite show no definite ratio of copper to iron, and the formula of the mineral is therefore written as $(\text{Cu}, \text{Fe})\text{SO}_4 \cdot 7\text{H}_2\text{O}$, representing an isomorphous mixture of melanterite and boothite.

Quartz Pseudomorphous after Apophyllite.—Some small crystals from Fort Point, San Francisco, with the form and angles of apophyllite, gave, on analysis, the results under V:

| | SiO_2 . | Al_2O_3 . | CaO . | MgO . | H_2O . | Total. |
|----|------------------|---------------------------|----------------|----------------|------------------------|---------|
| V. | 90·58 | 1·58 | 1·87 | 2·20 | 4·32 | 100·55. |

L. J. S.

The supposed presence of Germanium in Euxenite, Samarskite, &c. GABRIELE LINCIO (*Centr. Min.*, 1904, 142—149).—Mendeléeff's suggestion that ekasilicon (germanium) might be found to be present in complex minerals containing titanium, zirconium, and niobium led to the determination by Krüss (1888) of about 0·1 per cent. of germanium in euxenite, and by Chrustchoff (1892 and 1894) of 1·5 per cent. in samarskite and traces in tantalite, fergusonite, niobite, gadolinite, &c. The author has made a detailed examination of several samples of euxenite and samarskite from various localities, but failed to detect even a trace of germanium. Winkler had

previously also failed to detect the presence of germanium in a sample of euxenite. Krüss's preparations have been re-examined by the author and found to be free from germanium. The sources of error are fully explained. Germanium is therefore known to occur only in the sulpho-salts argyrodite, canfieldite, and franckeite. L. J. S.

Zeolites [Zeophyllite and Natrolite] from Gross-Priesen, Bohemia. ANTON PELIKAN (*Ber. Akad. Wien, Math.-Naturw. Cl.*, 1902, 111, (i), 334—347).—The name *zeophyllite* is given to a mineral occurring as hemispheres composed of radially arranged plates, which have a perfect cleavage with pearly lustre in one direction. Indistinct crystals are rhombohedral, and etched figures on the basal (cleavage) plane indicate tetartohedral symmetry. The central portion of a cleavage flake is uniaxial and negative, whilst the surrounding portions are optically biaxial; the latter, however, become uniaxial when the crystal is heated. Sp. gr. 2·764. The mineral is decomposed by hydrochloric acid with separation of silica. Analysis I, by E. Zdarek, gives the formula $H_4F_2Ca_4Si_3O_{11}$. Before the blowpipe, the mineral behaves like a zeolite, and many of its characters indicate a close relation to apophyllite.

| | SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | CaO. | MgO. | Na ₂ O. | K ₂ O. | H ₂ O. | F. | Total, less O for F. |
|-----|--------------------|----------------------------------|----------------------------------|-------|------|--------------------|-------------------|-------------------|------|----------------------------|
| I. | 38·84 | 1·73 | 0·10 | 44·32 | 0·17 | 0·38 | 0·24 | 8·98 | 8·23 | 99·52 |
| II. | 46·95 | 26·79 | — | 0·27 | — | 16·23 | 1·38 | 9·46 | — | 101·08 |

Zeophyllite occurs in association with apophyllite, natrolite, analcite, and calcite in cavities in felspar-basalt. Goniometric and optical determinations and an analysis (II) of the natrolite are given.

L. J. S.

Association of Natrolite and Datolite at Pokolbin, New South Wales. C. ANDERSON (*Records Australian Museum*, 1904, 5, 127—130).—A white, radially fibrous mineral occurring in cavities in an amygdaloidal hypersthene-andesite at Pokolbin, Co. Northumberland, was seen, on microscopical examination of thin sections, to consist of needles of natrolite with a second mineral in the interspaces. The variations in sp. gr. (2·27—2·54) and in composition (analyses I—IV) also point to the material being a mixture. One specimen (anal. IV), with much the appearance of the others, consists of natrolite alone; the others (I—III) are mixtures of natrolite and datolite.

| | SiO ₂ . | Al ₂ O ₃ . | CaO. | <u>K₂O.</u> | <u>Na₂O.</u> | B ₂ O ₃ . | <u>H₂O</u> (100°). | <u>H₂O</u> (>100°). | Total. |
|------|--------------------|----------------------------------|-------|------------------------|-------------------------|---------------------------------|----------------------------------|-----------------------------------|--------|
| I. | 43·47 | 16·07 | 14·54 | 8·96 | | 9·93 | 6·87 | | 99·84 |
| II. | 43·44 | 18·67 | 13·06 | 0·39 | 9·23 | [8·06] | 0·26 | 6·89 | 100·00 |
| III. | 44·25 | 23·47 | 8·43 | 11·57 | | [4·76] | 7·56 | | 100·00 |
| IV. | 46·91 | 27·10 | 0·63 | 0·14 | 15·65 | — | 0·34 | 9·38 | 100·15 |

L. J. S.

A New Variety of Orthoclase. LOUIS DUPARC (*Compt. rend.*, 1904, 138, 714—715).—Intergrown with albite in the granite of

Troitsk, northern Urals, is an orthoclase in which the acute bisectrix of the optic axes is perpendicular to the plane of symmetry and is positive in sign; the extinction on the plane of symmetry is $+6^\circ$ to $+9^\circ$. The same characters have also been rarely observed in the orthoclase of the protogine of the Alps. For this optically abnormal variety of orthoclase (*Fr. orthose*), the name *isorthose* is proposed.

L. J. S.

Lawsonite. WALDEMAR T. SCHALLER and WILLIAM F. HILLEBRAND (*Amer. J. Sci.*, 1904, [iv], 17, 195—197. Compare Abstr., 1896, ii, 370).—A crystallographic description is given of new material from the original locality, Marin Co., California, and two new forms noted. Analysis of carefully purified material of sp. gr. 3.121 gave the following results, which agree closely with the formula previously given, namely, $H_4CaAl_2Si_2O_{12}$. The blowpipe reactions of the mineral are given in detail.

| SiO ₂ . | TiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | MnO. | CaO. | MgO. | K ₂ O. | Na ₂ O. | H ₂ O (ignition). | Total. |
|--------------------|--------------------|----------------------------------|----------------------------------|------|-------|-------|------|-------------------|--------------------|------------------------------|--------|
| 38.45 | 0.38 | 31.35 | 0.86 | 0.10 | trace | 17.52 | 0.17 | 0.23 | 0.06 | 11.21 | 100.33 |

L. J. S.

Picrite and its Alteration Products. REINHARD BRAUNS (*Jahrb. Min., 1904, Beil.-Bd., 18, 285—334*).—A description is given of the Upper Devonian picrite of the neighbourhood of Dillenburg, Nassau; it differs from the Middle Devonian picrite of the same district in containing no primary hornblende. The original minerals are: olivine (anal. I), bytownite, augite (II), chromiferous magnetite (III), &c.; secondary minerals are: serpentine, radiotite (IV and V), webskyite, chlorite, pseudophite, fibrous augite and hornblende, garnet (VI), quartz, magnetite, hæmatite, calcite, aragonite, and apatite.

The name *radiotite* is given to a radially fibrous mineral occurring as aggregates of small spheres in the serpentine. In thin sections, it is colourless and transparent; the axis of greatest optic elasticity coincides with the length of the fibres. Analyses IV and V, by F. W. Küster, show that the new mineral has the same composition as serpentine ($Mg_3Si_2O_7 \cdot 2H_2O$), but it differs from this in not being attacked by hydrochloric acid and in its lower specific gravity of 2.70.

| | SiO ₂ . | TiO ₂ . | Al ₂ O ₃ . | Cr ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | MnO. | CaO. | MgO. | H ₂ O. | Total. | Sp. gr. |
|------|--------------------|--------------------|----------------------------------|----------------------------------|----------------------------------|-------|------|-------|-------|-------------------|--------|---------|
| I. | 39.45 | — | 0.21 | — | — | 18.88 | — | 1.28 | 39.47 | — | 99.29 | 3.36 |
| II. | 51.62 | 2.99 | 4.75 | 2.95 | — | 5.06 | — | 18.00 | 14.60 | — | 99.97 | 3.33 |
| III. | 6.40 | — | little | 8.88 | much | much | — | 2.78 | 5.43 | — | — | — |
| IV. | 41.48 | — | — | — | 8.40 | — | — | 1.50 | 35.84 | 11.96 | 99.18 | 2.70 |
| V. | 41.50 | — | — | — | 8.50 | — | — | 0.55 | 35.73 | 12.13 | 98.41 | |
| VI. | 35.05 | — | 0.32 | — | 30.34 | — | 1.06 | 32.52 | 1.78 | 1.32 | 102.29 | — |

L. J. S.

Eclogite-bearing Breccia from the Bingera Diamond Field. GEORGE W. CARD (*Records Geol. Surv. New South Wales*, 1902, 7, 29—39).—A petrographical description is given of the materials of a breccia filling a volcanic pipe at Ruby Hill, near Bingera, which presents many resemblances to the diamond-bearing breccia of South Africa (Abstr., 1899, ii, 769; 1901, ii, 251). The eclogite (analysis I)

is composed of garnet, pyroxene (omphacite, sp. gr. 3·338, anal. II), feldspar, and cyanite. Analyses, by H. P. White :

| | SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | MnO. | MgO. | CaO. | Na ₂ O. |
|-----|--------------------|----------------------------------|----------------------------------|------|-------|-------|-------|--------------------|
| I. | 43·05 | 20·74 | 4·55 | 4·08 | 0·23 | 7·06 | 15·30 | 1·59 |
| II. | 45·92 | 12·03 | 2·24 | 1·73 | trace | 13·30 | 22·73 | 1·19 |

| | K ₂ O. | H ₂ O. | TiO ₂ . | CO ₂ . | P ₂ O ₅ . | V ₂ O ₅ . | Total. |
|-----|-------------------|-------------------|--------------------|-------------------|---------------------------------|---------------------------------|--------|
| I. | 0·21 | 3·47 | trace | — | 0·02 | trace | 100·30 |
| II. | 0·32 | 0·66 | trace | 0·39 | — | trace | 100·51 |

L. J. S.

Gabbro-rocks of the Val Tellina. OTTO HECKER (*Jahrb. Min.*, 1903, *Beil.-Bd.*, 17, 313—354).—In the neighbourhood of Leprese, in the Upper Val Tellina, Lombardy, is a series of rocks of the gabbro family, which vary from olivine-gabbro to hornblende-gabbro and norite (and in one instance approaching to diorite) according to the relative amounts of the ferromagnesian minerals present, namely, diallage, brown hornblende (anal. V), olivine, rhombic pyroxene (VI), and biotite. Analyses of the feldspars of these rocks are given under I—IV. Several bulk analyses of the rocks themselves are also given.

| | SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | CaO. | MgO. | Na ₂ O. | K ₂ O. | Total. | Sp. gr. |
|------|--------------------|----------------------------------|----------------------------------|-------|-------|-------|--------------------|-------------------|--------|-------------|
| I. | 52·19 | 31·94 | — | — | 10·82 | — | 4·87 | 0·41 | 100·23 | 2·699—2·704 |
| II. | 52·10 | 30·60 | — | — | 12·22 | — | 4·80 | 0·20 | 99·92 | 2·724 |
| III. | 56·00 | 27·81 | — | — | 9·29 | — | 5·97 | 0·57 | 99·64 | 2·696 |
| IV. | 53·83 | 29·53 | — | — | 12·96 | — | 3·81 | 0·49 | 100·62 | 2·697 |
| V. | 48·04 | 8·98 | — | 16·44 | 6·72 | 18·87 | — | — | 99·05 | 3·269 |
| VI. | 50·76 | 5·86 | 0·49 | 11·39 | 15·19 | 15·19 | — | — | 98·88 | 3·230 |

L. J. S.

Coral-rock from Borings in the Funafuti Atoll. JOHN W. JUDD (*The Atoll of Funafuti*, *Royal Soc. Rep.*, London, 1904, 362—389).—The coral-rock is composed essentially of calcium and magnesium carbonates, with only small amounts of insoluble inorganic matter (usually less than 0·01 per cent.) and calcium phosphate (about 0·2 per cent.). The proportion of magnesium carbonate rises, in the first 50 feet of descent in the borings, from the normal of 1 to 5 per cent. up to a maximum of nearly 16 per cent., which is attained at a depth of about 25 feet, and then declines again to what may be considered the normal amount of 1 to 5 per cent. At 637 feet, the percentage of magnesium carbonate again rises from this normal, and by 660 feet has reached nearly 40 per cent. This proportion, with some small exceptions, is maintained to the bottom of the bore-hole at 1114 feet. The increase of magnesium carbonate in the higher levels is no doubt due to the leaching out of calcium carbonate by sea-water containing carbon dioxide, whilst the increase at greater depths is probably due to replacement of calcium by magnesium from the sea-water.

L. J. S.

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[Meteorites of Schafstädt, Pavlovka, and Linum.] CARL KLEIN (*Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 114—153).—A list is given of

the meteorites represented in the University collection at Berlin, with notes on those recently acquired.

Schafstädt, Merseburg.—This stone consists of leucite, anorthite, augite, glassy ground-mass, and ore, having the same composition as a leucite-tephrite. Leucite, which is present as icositetrahedra with twin-lamellæ, has not before been recognised as a meteoric mineral, and the name *leuciteuranolith* is given to this type of meteorite.

Pavlovka, Balachev, Russia.—This contains augite, bronzite, enstatite, olivine, anorthite, and perhaps leucite. Analysis, by Lindner, gave the results under I.

Linum, Brandenburg.—A chondritic stone with olivine, bronzite, augite, metallic iron, labradorite, and troilite. Analysis II.

| | SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | CaO. | MgO. | Na ₂ O. | K ₂ O. | MnO. | Metallic iron. |
|-----|--------------------|----------------------------------|----------------------------------|------|------|-------|--------------------|-------------------|------|----------------|
| I. | 50·91 | 6·30 | 12·74 | 5·95 | 6·24 | 14·69 | 2·04 | 0·43 | 0·30 | — |
| II. | 43·05 | 2·44 | — | 1·32 | 3·49 | 25·72 | 1·39 | 0·26 | 0·20 | 15·83 |

| | Iron combined with S. | Ni. | Cu. | S. | P. | TiO ₂ . | Cr ₂ O ₃ . | H ₂ O. | Total. | Sp. gr. |
|-----|-----------------------|------|------|------|------|--------------------|----------------------------------|-------------------|--------|---------|
| I. | — | 0·10 | 0·12 | — | — | 0·03 | — | 0·44 | 100·29 | 3·335 |
| II. | 3·23 | 0·71 | — | 1·85 | 0·07 | — | 0·31 | 0·12 | 99·99 | 3·542 |

Ternera, Atacama, Chile.—Analysis III.

| | Fe. | Ni. | Co. | S. | P. | Total. | Sp. gr. |
|------|-------|-------|------|------|------|--------|---------|
| III. | 82·17 | 16·22 | 1·42 | 0·13 | 0·11 | 100·05 | 7·694 |

L. J. S.

Physiological Chemistry.

Rhythms of Susceptibility and of Carbon Dioxide Production in Cleavage. E. P. LYON (*Amer. J. Physiol.*, 1904, 11, 52—57).—The fertilised egg of *Arbacia* is especially sensitive to the action of temperatures between 32° and 36° just before cleavage, and resistant 10—20 minutes later. Just after the first cleavage, it is again resistant, and susceptible just before the second. There are also resistant and susceptible periods to the effect of cold, and to lack of oxygen. The production of carbon dioxide is also rhythmic, the greatest amount being produced at the time of active cytoplasmic division.

W. D. H.

Permeability to Ions of Blood-corpuscles. RUDOLF HÖBER (*Pflüger's Archiv*, 1904, 102, 196—205).—Under the influence of carbon dioxide, the blood corpuscles of man and frog take on electrical properties which render their membrane permeable to anions. This fails in the absence of carbon dioxide. Cations like Fe^{+++} and Al^{+++} , which act like H^+ on anodic colloids, cause no permeability to

anions. The production of anion permeability is a reversible process. The blood of fresh water fish freezes at -0.558° . W. D. H.

Blood-platelets and Coagulation. K. BÜRGER (*Pflüger's Archiv*, 1904, 102, 36—94).—The blood-platelets are regarded as independently formed elements of the blood. Methods are described for obtaining them, and also for estimating the coagulation time of blood. Blood coagulation stands in the closest relationship to the breakdown of the platelets; they are believed to contribute directly to fibrin formation.

W. D. H.

Blood Coagulation. P. MORAWITZ (*Beitr. chem. Physiol. Path.*, 1904, 5, 133—141. Compare this vol., ii, 59).—A further contribution to a study of blood-coagulation, especially in reference to the varieties of pro-ferment. The principal new idea now introduced is that a *kinase* analogous to Pawloff's enterokinase is necessary to effect the change. A substance called thrombogen, when acted on by the kinase, yields a pro-ferment; this, when acted on by calcium ions, yields the ferment.

W. D. H.

Influence of Inhibiting Agents on the Coagulation of Bird's Plasma. ERNST FULD and KARL SPIRO (*Beitr. chem. Physiol. Path.*, 1904, 5, 171—190).—Blood plasma of the bird obtained after peptone injection coagulates on the addition of muscle extract; the time relationship of the clotting with varying quantities of extract follows Schutz's law very closely. As Wooldridge showed with dog's peptone plasma, it does not clot with fibrin ferment; the organ extracts contain some zymoplastic substance or metaferment which is probably the same as Morawitz's β -prothrombin. Investigations of leech extract plasma from birds, and the antagonism of "hirudin" towards organ extracts, yield complicated results. The question of what anti-substance is present in peptone plasma is also discussed. Morawitz's idea that a kinase is necessary is supported. The complexity of the subject is intensified by the introduction of a number of new terms (cytozyme, plasmozyme, holozyme, &c.), which sufficiently demonstrate the uncertainty of present theories.

W. D. H.

Blood Coagulation in Arthropods. LEO LOEB (*Beitr. chem. Physiol. Path.*, 1904, 5, 191—207).—In arthropods (crabs, lobsters, &c.), the so-called first coagulation is an agglutination of the corpuscles, and is inhibited by anti-agglutinating agents. It is analogous to the agglutination of blood-platelets in vertebrate blood. This is independent of the second coagulation, or formation of fibrin, although after a time the agglutinated corpuscles look like fibrin threads. The agglutinated mass has a strongly coagulating action on the fibrinogen of the plasma. The agglutinated cell masses of goose's blood have a similar action on invertebrate blood, but a relatively weak action on goose's blood-plasma. The action of tissue "coagulins" (from muscle, liver, lymph glands) is specific in both classes. These are rendered inactive by great dilution of the blood, although the blood clot will still produce coagulation. True fibrin formation does not, however, occur in all invertebrates. Leech extract has little or no

action on invertebrate blood. *In vitro*, Witte's peptone hastens the coagulation of goose plasma, and inhibits that of lobster plasma. Merck's peptone is in both cases almost inactive. Foreign substances, such as filter paper, hasten the clotting of vertebrate blood, but have no action on invertebrate blood. In all cases, the presence of calcium is important.

W. D. H.

Specific Erythrolysis. CLARENCE QUINAN (*Beitr. chem. Physiol. Path.*, 1904, 5, 95—109).—Diffusible material plays no part in erythrolysis; the blood proteids have no specific action. The hæmolytic action is attributed to specific colloidal substances, which act in the manner of enzymes.

W. D. H.

Oxidation and Reduction in Animal Organism. JOSEPH H. KASTLE and ELIAS ELVOVE (*Amer. Chem. J.*, 1904, 31, 195—207).—The research originated from the idea that changes of the nature of nitrification and denitrification can be brought about by higher as well as by lower organisms. The experiments were made on rabbits fed on oats; on this diet, their urine shows no reaction for nitrates or nitrites. Various substances were then injected subcutaneously. The results show that nitrous acid and nitrites are partially oxidised to nitrates, and that nitric acid and nitrates are partially reduced to nitrites. Corresponding results were obtained with higher plants. It is a striking fact how many poisons are either powerful oxidising or reducing agents; the following list contains examples: nitrates, chlorates, arsenates, nitrobenzene, picric acid, chromates, organic peroxides and peracids are toxic oxidising compounds. Nitrites, hydrogen sulphide, arsenites, aniline, phosphorus, phosphine, hydroxylamine, phenylhydrazine, benzene, toluene, terpenes, and other hydrocarbons, formaldehyde, acetaldehyde, and other aldehydes, methyl, ethyl, amyl, and other alcohols, catechol, resorcinol, quinol, pyrogallol are examples of toxic reducing substances. In this list, no oxidising substance is included but such as is known to be reduced in the organism, and no reducing substance but such as is known to undergo oxidation in the body. In a series of analogous compounds, toxicity and power to effect oxidation or reduction stand in the same order. It is further noted that many pathogenic organisms are anaërobic, or may be so; the growth of bacteria in an impoverished oxygen-supply often results in the development of toxins. Probably the toxins themselves belong to the class of reducing poisons.

W. D. H.

Absorption and Kataphoresis. RUDOLF HÖBER (*Pflüger's Archiv*, 1904, 101, 607—635).—A theoretical discussion of the factors concerned in absorption, and an attempt to explain it on physical grounds. Reid's objections to a theory of electro-osmosis are not considered fatal to its acceptance.

W. D. H.

Absorption and Assimilation of Iron. S. TARTAKOWSKY (*Pflüger's Archiv*, 1904, 101, 423—553. Compare this vol., ii, 189).—Further experiments which show that iron administered as a medicament is

really absorbed and assimilated, and is therefore available for hæmoglobin formation. In fact, it behaves in every way like the organic iron compounds of the ordinary food. A very complete review of previous work on the subject is given, and the views of others are discussed.

W. D. H.

Synthesis of Higher Fatty Acids in the Liver. O. HILDESHEIM and JOHN B. LEATHES (*Proc. Physiol. Soc.*, 1904, i—ii; *J. Physiol.*, 31).—Minced liver contains from 10 to 40 per cent. more fat after incubation in a current of moist air for 1—3 days than it does when fresh. Immersion of the flasks in boiling water prevents this increase. Putrefaction was hindered, but not wholly prevented, by antiseptics, but the organisms are not responsible for the increase of fatty acids. If glycogen is added to the flasks, the increase is still more marked.

W. D. H.

Influence of Castration on the Phosphorus of the Female Organism. FELIX HEYMANN (*Zeit. physiol. Chem.*, 1904, 41, 246—258).—A retention of phosphorus is described by some authors as a metabolic result of castration in female animals. This is incorrect, indeed in many cases the phosphoric acid in the skeleton is lessened. Lecithin is unaffected.

W. D. H.

Physiology of the Thymus. DIARMID NOËL PATON and ALEXANDER GOODALL (*J. Physiol.*, 1904, 31, 49—64).—In guinea-pigs, the thymus grows until the animal reaches the age of about two months, when the animal has an average weight of 300 grams, and is capable of reproduction; after this it degenerates. Removal of the organ has no influence on growth, or on the red corpuscles. There is a decrease in all varieties of leucocytes. When such animals become pregnant, leucocytosis occurs as usual. Infection with tubercle, injection of terabene (causing leucocytosis) produce the same effect as in normal animals; the resistance of the animals to the diphtheria toxin is unchanged. Injection of broth cultures of staphylococci and streptococci do not usually produce the marked leucocytosis seen in normal animals.

W. D. H.

Physico-chemical Behaviour of Liver Cells. EUGEN PETRY (*Beitr. chem. Physiol. Path.*, 1904, 5, 245—275).—An investigation of the effects of acids, alkalis, &c., on liver cells, similar to those carried out by others on blood corpuscles. The main point investigated is the permeability to chlorine, and the results are on the whole similar to those previously obtained with blood corpuscles.

W. D. H.

Secretion of Feather Glands. FRANZ RÖHMANN (*Beitr. chem. Physiol. Path.*, 1904, 5, 110—132).—The origin of fat from proteid is a much debated question. Some believe that it is proved by the formation of fat in the cells of the mammary and sebaceous glands; others, on histological evidence, believe this may be explained by the capacity of the cells to pick out the fat from the nutrient blood stream. In the present research the Bürzel glands of the bird were investigated;

although small quantities of glycerol are present, the principal alcohol is octadecyl alcohol, and the fatty acids present are combined as esters of this. Feeding experiments with various fats were carried out, and an alteration in the secretion and in the composition of the subcutaneous fat also were observed. Histological observations were also made. All the observations support the theory that a fatty degeneration of cell-protoplasm does not occur, but that the material is formed by simple chemical processes from the fat of the blood stream.

W. D. H.

Amount of Fat in Muscle. JOHN B. LEATHES (*Proc. Physiol. Soc.*, 1904, ii—iii; *J. Physiol.*, 31).—The figures given show that the red muscles of the rabbit, such as those of the diaphragm, soleus, and heart, contain a greater store of fat than the white muscles of the same animal or the mixed muscles of the cat.

W. D. H.

Composition of Bear's Fat. PAUL N. RAIKOW (*Chem. Zeit.*, 1904, 28, 272—273).—An analysis of bear's grease both from the belly and the kidneys. It transpired that the animal had fed chiefly on hazelnuts.

| | Belly fat. | Kidney fat. |
|-------------------------------------|------------|-------------|
| Sp. gr. at 15° | 0.9209 | 0.9211 |
| Melting point of insoluble acids... | 32—32.25 | 30.5—31 |
| Acid number..... | 2.2 | 2.2 |
| Ester number | 192.6 | 198.1—198.3 |
| Iodine number | 98.5 | 107.4—106.5 |
| Reichert-Meissl number | 1.66 | 1.15 |
| Refractometer degrees at 25° | 61.2 | 61.2 |
| " " 40° | 53 | 53 |

Once melted, the fat remained practically liquid at the ordinary temperature. There is little doubt that its peculiar properties are due to the fact that it was chiefly derived from hazel-nut oil. L. DE K.

Antitoxin Formation in Autolysis. LEON BLUM (*Beitr. chem. Physiol. Path.*, 1904, 5, 142—170).—Various organs were subjected to autolysis and the products examined for antitoxic substances. The toxins against which they were tested were cobra poison, diphtheria toxin, and tetanus toxin. The only positive result obtained was in the case of lymph glands, which on autolysis develop an antitoxin towards the tetanus poison. This is absent in the fresh gland. Details of its action are described in full.

W. D. H.

Physical Chemistry of Agglutinins. SVANTE ARRHENIUS (*Zeit. physikal. Chem.*, 1903, 46, 415—426).—This paper consists of an examination of the results already published by Eisenberg and Volk (*Zeit. Hygiene*, 1902, 40, 155—195) in order to show how they may be employed quantitatively. It is shown that the figures may be used in this way, and the formulæ deduced are of quite a simple character.

W. D. H.

Composition of Goat's Milk. PAUL BUTTENBERG and F. TETZNER (*Zeit. Nahr. Genussm.*, 1904, 7, 270—272).—The following table shows the composition of the milk of 5 goats of different ages. Each milk was examined separately and the analyses were made on 7 consecutive days :

| Age of Goat. | Time of milking. | Fat per cent. | Non-fatty solids per cent. |
|--------------|------------------|---------------|----------------------------|
| 5 years | { Morning | 2.1—2.5 | 7.13—7.71 |
| | { Evening | 2.3—2.8 | 7.37—7.59 |
| 3 years | { Morning | 2.5—3.4 | 8.01—8.43 |
| | { Evening | 3.0—3.9 | 8.18—8.52 |
| 2½ years | { Morning | 3.4—3.7 | 8.19—8.53 |
| | { Evening | 4.0—4.7 | 8.14—8.59 |
| 3 years | { Morning | 2.6—3.0 | 8.02—8.23 |
| | { Evening | 3.1—3.4 | 7.91—8.38 |
| 2 years | { Morning | 3.8—4.4 | 8.82—9.07 |
| | { Evening | 4.9—5.6 | 8.59—8.99 |

W. P. S.

Action of Chloral on the Secretion of Bile. ARTHUR FALLOISE (*Bull. Acad. Roy. Belg.*, 1903, No. 12, 1106—1129).—Chloral hydrate introduced in the dog's duodenum produces, after a latent period of 2 or 3 minutes, a remarkable acceleration of the flow both of bile and pancreatic juice ; the former persists for several hours, the latter for about 30 minutes. The persistence in the case of bile is due to the action of the absorbed drug on the liver cells ; this action has a latent period of 15—20 minutes. The early increase in the flow of both juices is due to the formation in the intestinal mucous membrane of a new substance (*chloral-secretin*) analogous to Starling and Bayliss' secretin. Chloral-secretin can also be prepared *in vitro* from the duodenal mucous membrane.

W. D. H.

Toxic Properties of Bile. MARC ARMAND RUFFER and MILTON CRENDIROPOULO (*J. Pathol. Bacteriol.*, 1904, 9, 278—310).—Bile is toxic not only for members of another species, but also for the same species. The principal effects studied were the inflammatory lesions at the point of subcutaneous injection and the effects on the blood. The latter are complex, for the groups of hæmolysins present are admixed with antibæmolytic (hæmosozic) substances.

W. D. H.

Excretion of Strontium. LAFAYETTE B. MENDEL and HENRY CLARKE THACHER (*Amer. J. Physiol.*, 1904, 11, 5—16).—Strontium salts are eliminated to a slight extent by the kidney, even although they are directly introduced into the circulation of animals (dogs, cats, rabbits). The excretion in the urine begins soon and ceases usually within 24 hours. Whatever be the manner in which the salts are introduced, the larger portion will be found in the fæces ; the place of excretion is apparently restricted to the region beyond the stomach. A functional relation to certain phenomena of peristalsis is suggested. The rate of elimination is slow and is influ-

enced by the amount of calcium in the food. Strontium is found deposited in the body chiefly in the bones, but traces are discoverable in the liver and muscles.

W. D. H.

Proteid in Urine. ADOLF OSWALD (*Beitr. chem. Physiol. Path.*, 1904, 5, 234—244).—The examination of the urine was made in cases of cyclic albuminuria. The proteid matter consisted of albumin and globulin. The globulin was mainly pseudoglobulin. In some cases, a precipitate was obtained by the addition of acetic acid; this does not consist of nucleo-proteid, but of euglobulin and fibrinogen (or fibrino-globulin). A small quantity of phosphorus found is attributed to contamination with lecithin.

W. D. H.

Behaviour of Uric Acid in Urine and the Effect of Alkalis on the Solubility of Uric Acid in Urine. FRANCIS H. MCCRUDDEN (*J. Amer. Chem. Soc.*, 1904, 26, 280—289).—A precipitate consisting of uric acid, or sodium urate, or a mixture of the two frequently separates from urine as it cools. The cause of this precipitation and the factors which determine the amount of uric acid remaining in solution have been widely discussed. It is now shown that the separation of uric acid is due to the concentration of the hydrogen ions being too great to permit of the presence of so large a quantity of negative uric acid ions. The fact that uric acid is not always immediately precipitated from cold urine is owing to the insoluble uric acid assuming the colloidal state. The effect produced on the equilibrium by the addition of small or large quantities of alkali and by changes of temperature is discussed. It is shown that by the addition of alkali to normal urine the solubility of uric acid in it would be increased at the temperature of the body, and that by the addition of considerable quantities of alkali to urine from which uric acid separates while still warm, its power of dissolving uric acid at the temperature of the body would also be increased. It is therefore suggested that in cases of uric acid calculi and gravel as much alkali should be administered as possible without making the urine alkaline.

E. G.

Excretion of Phloridzin. KÔTARÔ YOKOTA (*Beitr. chem. Physiol. Path.*, 1904, 5, 313—316).—After subcutaneous injection of phloridzin in rabbits, about 92 per cent. is recoverable as such in the urine. If the drug is given by the mouth, the amount recovered is less, probably owing to incomplete absorption. The existence of a lævorotatory substance, into which Cræmer believed part of the phloridzin is converted, is considered possible.

W. D. H.

Purine Substances in Human Fæces. J. WALKER HALL (*J. Pathol. Bacteriol.*, 1904, 9, 246—259. Compare Abstr., 1902, ii, 465).—On a mixed diet, the quantity of purine nitrogen in the fæces varies from 0.01 to 0.03 per diem. Medium amounts of meat and hypoxanthine added to the diet do not raise this figure, but excessive amounts of meat, thymus, or guanine do. In diarrhœa, the fæcal purine is increased; in rheumatism it is not. The fæcal purine originates from shed nuclein, bacteria, and intestinal secretions. The nuclein is to

some extent decomposed in the alimentary canal; the resulting adenine and guanine may be excreted as such, or may be oxidised to form xanthine and hypoxanthine.

W. D. H.

Milky Ascites in Carcinoma. HEINRICH WOLFF (*Beitr. chem. Physiol. Path.*, 1904, 5, 208—211).—Analytical details of the composition of the ascitic fluid in a case of abdominal cancer are given. Most interest attaches to its milky appearance; the fat-like material was shown to consist of an oleic acid ester of cholesterol, and is believed to have been chemically united to the euglobulin fraction of the proteids.

W. D. H.

Action of a Salt Solution in Locomotor Ataxy. SAMUEL A. MATTHEWS and ORVILLE H. BROWN (*Amer. J. Physiol.*, 1904, 11, 1—4).—The subcutaneous injection of a mixture of 250 c.c. of $m/8$ sodium chloride, 125 c.c. of $m/8$ sodium sulphate, 120 c.c. of $m/12$ sodium citrate, and 5 c.c. of $m/8$ calcium chloride in cases of locomotor ataxy causes pains similar to those felt in the early stages of the disease, even although it may have been years since the pains were felt. The pains decrease successively after each injection, until about the fourth or fifth, after which they may not occur at all. The procedure was found to have no therapeutic value, but the reaction may be of diagnostic value. The sensations are not elicited in normal individuals.

W. D. H.

Cytodiagnosis in Nervous Diseases. CHARLES L. DANA and T. W. HASTINGS (*Medical Record, New York*, 1904, Jan. 23).—The paper relates mainly to the examination of the cellular elements in the cerebro-spinal fluid of cases of nervous disease. The fluid was obtained during life by lumbar puncture. A point of chemical interest noted is that in two cases of alcoholic psychosis, choline was obtained from the fluid, in confirmation of Mott and Halliburton's statement.

W. D. H.

Action of Chemical Stimuli. HERMANN BRAEUNING (*Pflüger's Archiv*, 1904, 102, 163—184).—Acids act as stimuli in eliciting reflexes; they act in virtue of a diffusion process. Different acids of the same concentration act in relation to their diffusion coefficients. The negative ion in molecular solutions of acids has no important influence. Acids may be arranged in order of toxicity, beginning with the strongest as follows: hydrochloric, nitric, acetic, sulphuric.

W. D. H.

Antiseptic and Physiological Action of Persulphates. DIOSCORIDE VITALI (*Chem. Centr.*, 1904, i, 749—750; from *Boll. Chim. Farm.*, 43, 5—11. See this vol., ii, 366).

Resolution of Salol in the Organism. VALERIO LUSINI (*L'Orosi*, 1903, 26, 47—51).—The author has made a number of experiments to determine what products in the organism bring about the resolution of salol into phenol and salicyclic acid, to which it owes its therapeutical value. To obtain the salol germ-free, it was dissolved in ether or chloroform, and after some time the solvent was distilled

off in a vacuum in sterilised vessels. Salol is decomposed by germ free pepsin or pancreatin; the latter is especially active and acts not only in aqueous solution, which may or may not be rendered alkaline, but also in presence of lactic acid or egg albumin. It is also resolved when left in contact with the faeces either of herbivorous animals or of man. *Bacillus coli* rapidly attacks salol, while the typhoid bacillus has very little action. Acid urine also decomposes salol in spite of the fact that it retains its acid reaction. Salol is also resolved by the blood, the serum of which, however, plays no part in the action; the decomposition is brought about only by the morphological elements—mainly by the white corpuscles—and if a protoplasmic poison such as quinine dihydrochloride is present, no action occurs. T. H. P.

Fate of Cyclic Terpenes and Camphor in the Animal Organism. V. Behaviour of Sabinol. EMIL FROMM (*Zeit. physiol. Chem.*, 1904, 41, 243—245. Compare Abstr., 1902, ii, 341).—Sabinol leaves the body in union with glycuronic acid; this glycuronic acid is the ordinary acid. The semicarbazone derived from it melts at 202—206°, not at 188° as Giemsa (Abstr., 1901, i, 11) stated. W. D. H.

Cryogenine and its Elimination. RÉNE COURAUD (*J. Pharm. Chim.*, 1904, [vi], 19, 344—347).—One hundred parts of the respective solvents dissolve the following weights of cryogenine: acetic acid, more than 100; amyl alcohol, 11·27; acetone, 7·31; ether of 65°, 2·77; water, 2·53; light petroleum, 0·78; chloroform, 0·78; anhydrous ether, 0·026; benzene, insoluble.

Cryogenine was isolated in the crystalline state from the urine voided during 5 days by a healthy man to whom a daily dose of 0·50 gram was administered.

Cryogenine is best detected in the urine by adding to 10 c.c. of it a few drops of phosphomolybdic acid; a blue coloration is obtained with more or less of a green tinge; sometimes a blue precipitate is formed as well. By testing the urine in this way, it was found that a single dose of cryogenine was eliminated from the system in a very short time (about 1½ days); whereas after 5 successive daily doses the elimination was not completed until 4 days had elapsed since the last dose. C. F. B.

Diuretic Action of 1:3-Dimethylxanthine. HEINRICH DRESER (*Pflüger's Archiv*, 1904, 102, 1—35).—Particulars are given of the course and amount of the diuresis produced by 1:3-dimethylxanthine as contrasted with that of other diuretics. Tables and illustrative diagrams are given. W. D. H.

Pupil Dilatation caused by Adrenaline. S. J. MELTZER and CLARA MELTZER AUER (*Amer. J. Physiol.*, 11, 28—36, 37—39, 40—51).—Details of experiments on cats and rabbits relating to the paradoxical pupil dilatation which is caused by subcutaneous injection of adrenaline, and which occurs only when the sympathetic is cut or the superior cervical ganglion removed. W. D. H.

Nicotine Poisoning in Rabbits and Guinea-pigs. ROBERT A. HATCHER (*Amer. J. Physiol.*, 11, 17—27).—Nicotine is uncertain in its action. Death is due to failure of respiration, and artificial respiration to be effective must be commenced before the respiratory centre is markedly depressed. Heat antagonises the toxic effect. No cumulative effects are seen when nicotine is given daily for several days. Nutritional disturbances follow its prolonged use, as is indicated by loss of weight, and the appearance of ulcers near the seat of injection. The preparation of an antitoxic serum was not found to be practicable. The average fatal dose for an adult rabbit is 20 mg. per kilo. of body weight; in the adult guinea-pig this number is 40, but in very young guinea-pigs it is 15.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Nitrifying Organisms. E. BOULLANGER and L. MASSOL (*Ann. Inst. Pasteur*, 1904, 18, 181—196. Compare Abstr., 1903, ii, 679).—The nitrous organism accommodates itself to all the ordinary carbonates, nitrification taking place when magnesium carbonate was replaced by calcium, barium, strontium, zinc, lead, nickel, manganese, copper, iron, or bismuth carbonate. Nitrification took place when the following ammonium salts were employed: arsenate, nitrate, nitrite, borate, bromide, carbonate, chloride, fluoride, thiosulphate, phosphate, sulphite, sulphide, acetate, formate, lactate, malate, succinate, tartrate, urate, and ammonium magnesium phosphate. Ammonium arsenite, iodide, citrate, and oxalate are only nitrified in solutions containing 0.5—1.0 gram per litre.

Hydroxylamine hydrochloride is not attacked by the nitrous organism. The nitric organism oxidises nearly all nitrites in solutions containing 0.5—1 gram per litre.

Experiments on the action of the nitrous organism on ammonium sulphate showed that there was a period of incubation which lasted six days, during which no nitrate was found. In the case of the nitric organism, this period was only two days.

Ammonium salts hinder the multiplication of nitric organism, but unless present in considerable quantity have no retarding action on the oxidising function of existing nitric organisms. Under ordinary conditions, the amount of ammonia in the soil can rarely be sufficient to interfere with the multiplication of the nitric organism. In solutions, the minimum retarding amount was found to be about two per million.

N. H. J. M.

Supposed Formation of Nitrogen by Fermentation with Putrefactive Bacteria. CARL OPPENHEIMER (*Zeit. physiol. Chem.*, 1904, 41, 3—7).—A series of errors in calculation is pointed out in Schittenhelm and Schröter's investigations (this vol., ii, 139). The

greater part of the residual gas described as nitrogen was in reality the excess of oxygen previously added. The conclusions drawn as to the evolution of nitrogen are valueless. J. J. S.

Gelatin Surface-colonies of *Bacillus Coli Communis*. WILLIAM G. SAVAGE (*J. Pathol. Bacteriol.*, 1904, 9, 347—358).—It is not possible to diagnose this organism from its surface-colonies only, for other organisms may simulate these, and the colonies of the *B. coli* are not always typical. W. D. H.

Agglutination in Dysentery. R. TANNER HEWLETT (*Trans. Pathol. Soc. London*, 1904, 55, 51—55).—There appear to be at least two strains of the *Bacillus dysenteriae*, with a profound difference in agglutinative properties. The value of the agglutination test in dysentery and the specificity of the bacillus are therefore still questions for the future. W. D. H.

Bacteria which are able in Absence of Light to utilise Carbon Dioxide as Source of Carbon. MARTINUS W. BEYERINCK (*Centr. Bakt. Par.*, 1904, ii, 11, 593—599).—The results obtained by Natanssohn (*Mitt. Zool. Stat. Neapel.*, 1903, 15, 655), showing that bacteria occur in the sea which reduce carbon dioxide by oxidation of hydrogen sulphide or thiosulphates, are confirmed. It was also found that sodium tetrathionate in presence of sodium carbonate yields sodium sulphate, sulphur, and carbon dioxide. Sodium dithionate was not attacked.

A bacterium, *Thiobacillus denitrificans*, was obtained from ditch water, which utilises free sulphur, converting carbonates and nitrates into sulphates with liberation of carbon dioxide and nitrogen.

N. H. J. M.

Bacterial Origin of the Gums of the Arabin Group. R. GREIG SMITH (*Centr. Bakt. Par.*, ii, 1904, 11, 698—703).—Cultivations of *Bacterium acacie* and *B. metarabinum* in media containing sucrose and asparagine produced acetic acid and a small amount of formic acid, together with *l*-lactic acid, a little succinic acid, and traces of oxalic acid. Tannic acid was also found.

B. acacie was found in the gum of plum trees and cedar, in peach trees, and in the gum of almond and Japanese date trees. *B. levaniiformans* was found in peach and Japanese date tree gum. The gum of peach trees is possibly in part produced by *B. Persicae*, which was also found.

The gum in the fruit of *Sterculia diversiola* consists of arabin and parabin, produced respectively by *B. acacie* and *B. parabinum*. Several varieties of the latter occur, all of which produce parabin mucus.

In experiments with peach, almond, and *Cedrela australis*, an organism (*B. Persicae*) was obtained which produces mucus on sucrose-potato-agar and in solutions containing sucrose. The mucus, when hydrolysed, yielded galactose and arabinose. During the fermentation of sucrose, carbon dioxide and alcohol were produced together with butyric and lactic acids and some acetic acid. Traces of succinic and formic acids were also found.

N. H. J. M.

Diplococcus Rheumaticus. JAMES M. BEATTIE (*J. Pathol. Bacteriol.*, 1904, 9, 272—277).—In two cases of acute rheumatism, the observations recorded confirm the results of Poynton and Paine in ascribing to a diplococcus the causation of the disease.

W. D. H.

Agglutination of Vibrios. MILTON CRENDIROPOULOU and Miss B. SHELTON AMOS (*J. Pathol. Bacteriol.*, 1904, 9, 260—271).—In cholera patients, several groups of vibrios are found, one only of which is regarded as the true cholera vibrio. The agglutinins of normal and specific serum are not the same. The agglutination of the cholera vibrio by its own specific serum is greatly favoured by the presence of calcium chloride, whereas this is not the case with other vibrios. Special attention is directed to the action of salts on agglutination; some inhibit and others favour the secretion of the agglutinable material by the micro-organisms.

W. D. H.

Preparation of Nutrose-Agar. S. W. H. EYRE (*Trans. Path. Soc. London*, 1904, 55, 91—105).—Full technical details for the preparation of this culture medium are given.

W. D. H.

Formation of Nitrous Acid in the Air confined in Arable Land. Nitrification by Chemical Processes in the Soil. FAUSTO SESTINI (*L'Orosi*, 1904, 27, 1—9).—It has been stated by Bonnema (*Chem. Zeit.*, 1903, 27, 149) that the formation of nitrous acid in soil is due not to the action of bacteria on atmospheric nitrogen, but to the oxidation of the latter by the ferric hydroxide present in the soil. The author finds, however, that it is not the nitrogen of the atmosphere, but the traces of ammonia contained therein, which undergoes oxidation, yielding nitrous acid; this reaction proceeds in presence of 0.2 per cent. of mercuric chloride or of large quantities of thymol. The nitrous acid formed serves as a food for, but is not produced by, nitric bacteria.

Griess's reagent is capable of reacting with a solution containing only 1 part of sodium nitrite in 30,000,000 of water; a sulphuric acid solution of *m*-phenylenediamine gives a coloration with 1 part of the salt in 1,000,000 of water, but not with 1 part in 10,000,000.

T. H. P.

Gaseous Exchange between the Atmosphere and Plants separated from their Roots and kept in the Dark. MARCELLIN BERTHELOT (*Compt. rend.*, 1904, 138, 602—607. Compare *Compt. rend.*, 1904, 138, 16).—The experiments described in this paper were conducted on a species of prairie grass cut in September, 1903, piled in heaps and covered to avoid loss by evaporation; daily observations made during nineteen days on the difference between the temperature of the middle of the mass and that of the air, and on the composition of the air withdrawn by means of an aspirator from the interior of the heap, showed that the chemical action due to ferments and microbes is accompanied by a development of heat, the temperature rising to 53° at the end of a week, and then gradually falling to that of the

air (17—21°) at the end of the third week. The air withdrawn from the interior of the heap consists of carbon dioxide, oxygen, and nitrogen only, the sum of the first two constituents being approximately the same as the volume of oxygen in normal air (20—23·1 per cent.), whilst the relative volume of nitrogen does not differ by more than 2·3 per cent. from that of ordinary air. These results show that the gaseous exchange between the atmosphere and the plants is similar to that which characterises animal respiration, (1) the amount of carbon dioxide formed being equal to the amount of oxygen used up, and (2) there being no production of ammonia or liberation of free nitrogen. Under the conditions of the experiment, the nitrogen is converted into urea or ammonium carbonate, for on repeated distillation of the material with excess of water, crystalline ammonium carbonate was obtained.

These results were confirmed by the ultimate analysis of the material before and after the experiment. M. A. W.

Toxic Action of Acids and Salts on Seedlings. (A Correction.) FRANK K. CAMERON (*J. Physical Chem.*, 1904, 8, 131).—In a paper on the above subject (this vol., ii, 283), it was stated that the increase of the toxic effect of acids on clover seedlings by the addition of potassium salt was the only instance observed where the addition of a *second* electrolyte did not cause a decrease of toxic effect. It is now pointed out that the author had previously observed some similar cases; for example, sodium chloride causes an increase of the toxic action of sodium sulphate on lupin seedlings, and a few other examples are given. L. M. J.

Choline in Plant and Animal Organisms. HEINRICH STRUVE (*Annalen*, 1904, 330, 374—379. Compare Abstr., 1902, ii, 636).—Since the discovery of Florence's test for choline (Abstr., 1900, ii, 328), which depends on the formation of crystals of iodocholine when a solution of potassium iodide is added to choline, the recognition of this base has become easy. By this means, it has been shown to occur in three forms in most animal and vegetable organisms: (i) in compounds soluble in ether, lecithin, (ii) in compounds soluble in water, (iii) in compounds with proteids.

The test is applied to the first class of compounds by evaporating the ethereal extract, decomposing the lecithin with sulphuric acid, evaporating with calcium hydroxide, extracting with alcohol, and then applying the test to the residue from the alcohol under the microscope. Choline is readily detected in substances soluble in water. The compounds of choline with proteids must first be separated from fat (lecithin), and secondly from choline compounds in aqueous solution; the choline is then set free by treatment with sulphuric acid or by alcoholic ammonia.

The author's observations have led to the following conclusions: (i) choline is found in the cell-protoplasm in all three forms; (ii) the choline of organic extracts soon disappears under the influence of micro-organisms, to be again formed by these organisms; (iii) all

diseases which are characterised by marked cellular growth are accompanied by excretion of choline; (iv) an animal organism does not normally excrete choline; (v) the formation of choline (or lecithin) is not entirely dependent on the presence of phosphoric acid; boric acid can take the place of the phosphoric acid. K. J. P. O.

The Evolution of Terpenoid Compounds in the Vegetable Organism. EUGÈNE CHARABOT and ALEXANDRE HÉBERT (*Ann. Chim. Phys.*, 1904, [viii], 1, 362—432).—A detailed account of work already published (compare Abstr., 1901, ii, 183, 619; 1902, ii, 99, 346, 523; 1903, ii, 172, 233, 505, 607). M. A. W.

Enzymes in the Sugar Beet. JULIUS STOKLASA, JOHANN JELÍNEK, and EUGEN VÍTEK (*Zeit. Zuckerind. Böhm.*, 1904, 28, 233—243. Compare Abstr., 1903, ii, 320, 388, and 746).—The authors show that after anaërobic respiration under a pressure of 350 atmospheres, the sugar beet yields a pressed juice containing invertase.

They have also continued their experiments on the zymase present in sugar beets which have been allowed to respire for some time under water. The beets were pounded, the pasty mass subjected to a pressure of 100 atmospheres, and the juice drawn off, the residue being then submitted to 400 atmospheres pressure and the juice again collected. The fermentative powers of these two samples of juice were found to be approximately equal. The fermentations were carried out in presence of antiseptics, and when 2 per cent. potassium meta-arsenite solution was employed, only in three cases was a slight growth of hyphomycetes and bacteria observed. As with yeast zymase, filtration of the juice through a Chamberland filter causes considerable diminution in its fermentative power, whilst when sterile sand is employed as filtering medium this power is only slightly decreased. T. H. P.

Vetches in Cereal Meal and in Human Food. ALBERTO SCALA (*Chem. Centr.*, 1904, i, 530; from *Staz. sper. agrar. ital.*, 36, 695—716).—Vetches, when dried at 90°, lost 7·65—12·24 per cent. of water. The percentage composition of the dried substance was as follows: nitrogenous matter (*a*, total), 17·7—27·3; (*b*, soluble), 6·0—7·2; albumin, 6·0—6·8; legumin, 6·8—12·0; fat, 1·0—1·3; wood, 3·7—10·7; starch, 64·8—68·8; pentosans, 3·4—5·5; non-nitrogenous extract (free from minerals), 7·2—8·9; and ash, 2·3—2·8.

Vetches are free from poisonous matter, and any objectionable taste is removed by sulphurous acid without any considerable loss in nutritive value. Vetch meal, when mixed with cereal meal or with 4—5 parts of gluten, may be used (in Italy) for making bread.

The methods of Voyle, Robine, Donny, and Valenti for detecting vetch meal are unsuitable for quantitative estimations. The legumin method, digestion for 12 hours with 4 per cent. sodium chloride solution, is preferable. N. H. J. M.

Analytical Chemistry.

Burette arranged to Fill and Level to an Automatic Zero and to return Unused Liquid to the Reservoir. ALVERGNAT-CHABAUD (*Bull. Soc. chim.*, 1904, [iii], 31, 349—350).—The burette proper is provided with a two-way cock (one passage of which serves for titrating purposes) and communicates both by a side-arm near its mouth and by the second passage of the two-way cock with a tube parallel to itself, which passes to the bottom of the closed reservoir holding the liquid. The cork of the reservoir also carries a tube provided with a caoutchouc ball, which, when pressed, forces the solution into the burette. The apparatus is figured in the original.

T. A. H.

Detection and Estimation of Iodides in the presence of Bromides and Chlorides by means of Potassium Iodate. HUGO DITZ and BENJAMIN M. MARGOSCHES (*Chem. Zeit.*, 1904, 28, 271—272).—A question of priority. The qualitative process communicated by Benedict and Snell (*Abstr.*, 1903, ii, 750) is practically the same as that given by the authors (*Abstr.*, 1902, ii, 12). A quantitative estimation based on the use of potassium iodate will be published in due course. [Benedict and Snell have since published their quantitative process (this vol., ii, 146).]

L. DE K.

Estimation of Sulphuric Acid. RICHARD SILBERBERGER (*Monatsh.*, 1904, 25, 220—248. See this vol., ii, 342).

Antiseptic and Physiological Action of Persulphates and their Toxicological Detection. DIOSCORIDE VITALI (*Chem. Centr.*, 1904, i, 749—750; from *Boll. Chim. Farm.*, 43, 5—11).—The antiseptic action of persulphates is only small, and in larger doses they are poisonous. Added to urine they retard the action of urea bacilli, but do not prevent mould formation. The author gives the following test for the detection of persulphates in urine. Addition of potassium iodine liberates iodine. After precipitating with lead acetate, the filtrate becomes turbid on heating and turns yellow. Basic lead acetate gives a precipitate which turns blue when treated with acetic acid and tincture of guaiacum. After precipitating with barium chloride, a further precipitate is obtained on boiling. Hydrogen sulphide causes a turbidity on warming. On adding potassium dichromate and sulphuric acid and shaking with ether, the latter turns dark blue. On heating with a trace of aniline, a brownish-black colour is obtained. Strychnine nitrate causes a crystalline precipitate. When heated with tincture of guaiacum, the mixture turns dark blue.

In cases of suspected poisoning by persulphates it is, however, the vomit which should be subjected to analysis, as there is little chance of finding any persulphate in the blood, urine, or intestines.

L. DE K.

Estimation of Carbon Dioxide in the Air. B. SWAAB (*Chem. Centr.*, 1904, i, 745—746; from *Chem. Weekblad.*, 1904, 177—182, 189—192).—Haldane's apparatus (Abstr., 1901, ii, 477) is strongly recommended.
L. DE K.

Estimation of Nitrites in Waters. J. DESFOURNEAUX (*Ann. Chim. anal.*, 1904, 9, 68). LUCIEN ROBIN (*ibid.*, 96).—Desfourneaux describes a method based on the liberation of nitrous acid by salicylic acid in the presence of potassium iodide and titration of the iodine thus set free.

Robin calls attention to his own process published in 1898 (Abstr., 1898, ii, 542), which is practically the same as that of Desfourneaux, acetic acid being used instead of salicylic acid.
L. DE K.

Use of Antipyrine in Analysis (Nitrite Reactions). C. REICHARD (*Chem. Zeit.*, 1904, 28, 339—340).—A criticism of Schuyten's process (Abstr., 1897, ii, 596). The author thinks this an excellent method for the detection of minute traces of nitrous acid. The coloration produced by an acetic acid solution of antipyrine is not, however, always of the same shade and, therefore, is less suitable for quantitative purposes. Acids other than acetic have also been tried, but without any better result.
L. DE K.

Estimation of Citrate-soluble Phosphoric Acid in Basic Slags. R. SORGE (*Zeit. angew. Chem.*, 1904, 17, 393—397).—An adverse criticism of the method accepted by the "Verband landwirtschaftlicher Versuchsstationen in Deutschen Reiche" for the separation of the silicic acid when testing basic slags.
L. DE K.

Estimation of Carbon Dioxide in the presence of Chlorine. MAX SCHLÖTTER (*Zeit. angew. Chem.*, 1904, 17, 301—302).—The author uses his hydrazine sulphate reaction (this vol., ii, 146) for the estimation of chlorine in electrolytic chlorine. One hundred c.c. of the gas are treated in a Bunte-burette with solution of hydrazine sulphate, and the diminution in volume multiplied by two represents the volume of chlorine. After withdrawing the hydrazine solution, the volume of carbon dioxide may be estimated as usual.

The process gives results which agree fairly well with those obtained by the more complicated Offerhaus process (this vol., ii, 86).

L. DE K.

Direct Estimation of Free Carbon Dioxide in Natural Waters. A. MCGILL (*J. Amer. Chem. Soc.*, 1904, 26, 183—186).—The estimation of free carbon dioxide in natural waters should be made at the source in order that accurate results may be obtained. A method suitable for this purpose is described. The carbon dioxide is removed from the water by bubbling air (previously freed from carbon dioxide) through it, and is afterwards led slowly into a series of small bottles which are nearly filled with solid glass beads and contain $N/100$ barium hydroxide

solution coloured with phenolphthalein. The number of bottles in which the colour is discharged gives an approximate measurement of the carbonic acid present in the volume of water operated on.

E. G.

Precipitation of Magnesium Oxalate with Calcium Oxalate. NICHOLAS KNIGHT (*Chem. News*, 1904, 89, 146—147).—In the analysis of dolomite, it was found that the magnesium oxalate precipitated with the calcium oxalate varied from an almost inappreciable amount to a considerable quantity. Using 1 gram of dolomite for the estimation, and, after removal of silica, iron, and alumina, precipitating the calcium with a slight excess of $N/2$ ammonium oxalate solution, the calcium oxalate when filtered at the end of 12 hours contained on an average 0.18 per cent. of magnesia. Before precipitating the iron and aluminium, about 2 grams of ammonium chloride were added. In cases where the calcium oxalate was not allowed to remain before filtering, the amount of magnesia in it increased to 1.2 per cent. It is therefore necessary to dissolve the unwashed calcium oxalate precipitate in hydrochloric acid, and then to add ammonia to reprecipitate the calcium oxalate, the two filtrates being united for the estimation of the magnesium.

W. P. S.

Titration of Ferric Iro. LUIGI CARCANO and RODOLFO NAMIAS (*Chem. Centr.*, 1904, i, 754—755; from *Boll. Chim. Farm.*, 43, 54—56).—In estimating ferric iron with potassium iodide in the presence of hydrochloric acid, there is some risk of the reaction being reversed. This, according to the authors, may be prevented by adding about 5 c.c. of chloroform, which, on shaking, removes the bulk of the liberated iodine from the solution. The whole is then titrated as usual with thiosulphate, using starch as final indicator.

L. DE K.

Colorimetric Estimation of Chromium. A. MOULIN (*Bull. Soc. chim.*, 1904, iii, 31, 295—296).—The author has applied the colour reaction between diphenylcarbazide and chromic acid observed by Cazeneuve (*Abstr.*, 1900, ii, 627; 1901, i, 655, and ii, 626) to the estimation of chromium. The diphenylcarbazide solution is prepared by dissolving 2 grams of this substance in 100 c.c. of alcohol (90°), to which 10 c.c. of acetic acid have been added, and diluting to 200 c.c. with alcohol. The standard chromic acid solution contains 0.00005 gram of the acid per c.c.

The chromium compound under investigation is first converted into potassium chromate; for this purpose, oxidation by hydrogen peroxide in presence of potassium hydroxide is recommended, the liquid being finally neutralised with acetic acid.

The estimation is carried out in the usual manner with the precautions that excess of the diphenylcarbazide solution is employed and that the chromate solution under investigation is made approximately of the same strength as the standard chromic acid solution.

T. A. H.

Separation of Chromium and Vanadium. PAUL NICOLARDOT (*Compt. rend.*, 1904, 138, 810—812).—In the absence of much iron, chromium can be separated from vanadium by converting it into chromyl chloride; for this purpose, the mineral is fused with excess of potassium chlorate and the small quantities of iron and magnesium separated in the ordinary way; the mixture of alkali chlorides, chromates, and vanadates is then treated with fuming sulphuric acid at a temperature of 60°, the chromyl chloride distills off, and the last traces are removed by means of a current of dry air; the vanadium in the residual liquid is treated with alcohol and finally titrated with permanganate.

If much iron is present (ferrochromovanadium irons, steels, &c.), the separation of the chromium and vanadium is effected by treating the compound with hydrochloric acid, oxidising the solution with nitric acid, and evaporating until the greater quantity of the acid is driven off, when the iron oxide is precipitated, carrying the vanadium with it, the chromium remaining in solution (compare Abstr., 1902, ii, 22). The vanadium is separated from the iron by first washing with ammonia and then fusing with alkali salts, and estimated volumetrically.

M. A. W.

New Test for Molybdenum. EM. LECOCQ (*Chem. Centr.*, 1904, i, 836; from *Bull. Assoc. Belge des Chimistes*, 17, 412—414).—Diphenylcarbazine has been recommended by Cazeneuve (Abstr., 1900, ii, 627) as a delicate test for some metals, such as copper, mercury, and iron. The author has tried its effect on molybdenum. If a drop of an alcoholic solution of the reagent is added to 40 c.c. of a weak solution of ammonium or sodium molybdate acidified with two drops of hydrochloric acid, the liquid turns indigo-violet, and on adding more of the reagent a violet precipitate is formed. Tungsten, titanium, and vanadium give no reaction. The test works best with an alcoholic solution which has been kept for some time. When substituting other alcohols for ethyl alcohol, colours of a different shade are obtained.

L. DE K.

Estimation of Titanium in Iron Ores. S. BURMAN (*Chem. Centr.*, 1904, i, 970; from *Stahl. u. Eisen*, 24, 302).—From half to one gram of the powdered ore is ignited for 45 minutes in a current of hydrogen and the reduced mass is boiled with 200 c.c. of water and 10 c.c. of hydrochloric acid. The undissolved matter is fused in a platinum crucible with ten times the bulk of soda (? sodium hydroxide), the fused mass is treated with water, and the insoluble matter washed with dilute soda solution. It is dissolved in hydrochloric acid, reprecipitated by addition of soda, and, finally, heated in a weighed platinum crucible with 10 grams of potassium hydrogen sulphate until dissolved. The mass is then dissolved in 400 c.c. of water, 10 grams of sodium metasilphite are added, the bulk of the acid is neutralised, and the titanium precipitated as orthohydrate by boiling with addition of sodium acetate. It is collected, washed, ignited, and weighed as oxide. It is liable to be contaminated with platinum. To what extent this has occurred may be fairly judged by

reweighing the platinum crucible after the fusion with potassium hydrogen sulphate.

L. DE K.

Electrolytic Analysis of Gold. F. MOLLWO PERKIN and W. C. PREBBLE (*Electro-Chem. Metall.*, 1904, 3, 490—494).—Gold may be deposited in a very satisfactory manner from solutions of gold salts in ammonium thiocyanate. With currents of 0.2 ampere per sq decimetre and 2 volts, the deposition of 0.05 to 0.08 gram is complete in from 5 to 6 hours at the ordinary temperature. With a current of 0.5 ampere, the time is shortened to $1\frac{1}{2}$ to 2 hours. A solution of 5 grams of ammonium thiocyanate in about 70 c.c. of water is heated to a temperature of 30° or 40°, the gold solution is slowly added, and the deposition proceeded with. The total bulk of solution employed should be from 120 to 150 c.c.

The deposit of gold may be removed from the electrode in a few minutes by means of a solution containing 2—3 grams of potassium cyanide, and 5 c.c. of hydrogen peroxide in about 100 c.c. of water. In most of the experiments described, gauze flag electrodes were used, but platinum basins were also employed.

W. P. S.

Iodine Absorption of Oil of Turpentine. ROBERT A. WORSTALL (*J. Soc. Chem. Ind.*, 1904, 23, 302—303).—Fifty-five samples of undoubtedly pure oil of turpentine had an average iodine absorption (Hübl) of 384. The absorption was found to be completed in from 4 to 6 hours, when about 3 times the total quantity of iodine necessary for complete saturation had been added. The iodine absorptions of the most common adulterants of oil of turpentine are: rosin spirits, 185; rosin oil, 97; kerosene, 0; naphtha, 0; "wood turpentine," 212; and "water-white wood turpentine," 328. The two latter are now largely manufactured, and appear to consist of both terpenes and alcoholic substances.

W. P. S.

Estimation of Prussian Blue. CH. COFFIGNIER (*Bull. Soc. chim.*, 1904, [iii], 31, 391—396. Compare Abstr., 1902, i, 664, and Wyrouboff, Abstr., 1904, i, 18).—Solutions of Prussian blue in mixtures of aliphatic alcohols with hydrochloric acid solidify without change of colour when cooled to low temperatures. On addition of water, the Prussian blue is reprecipitated. It is proposed to utilise this reaction for the estimation of this colouring matter in commercial "blues" containing as diluents starch, barium sulphate, &c. About 2 grams of the material are treated with 100 c.c. of a mixture of propyl alcohol and hydrochloric acid, and when the whole of the Prussian blue has dissolved, the mixture is made up to 200 c.c. with the same solvent. If the diluent is soluble, for example, starch, 100 c.c. of the solution are treated with a sufficient quantity of water to completely precipitate the blue; if the diluent is insoluble, 100 c.c. of the filtrate are treated in like manner. The quantity of water necessary to ensure complete precipitation decreases fairly regularly with the increase of concentration of the Prussian blue solution.

In powders containing alumina as a diluent, the solution of the blue takes place slowly, and is only complete after protracted ebullition.

The filtrate from the precipitated Prussian blue always contains some ferric chloride owing to the presence of traces of this salt in many of the Prussian blues of commerce, and also to a slight but negligible decomposition of the colouring matter by the hydrochloric acid.

T. A. H.

Estimation of Cyanates. THOMAS EWAN (*J. Soc. Chem. Ind.*, 1904, 23, 244).—The estimation of a cyanate in presence of cyanide by precipitation as silver salt is found to be unsatisfactory owing to (a) the relatively large solubility of silver cyanate, (b) the difficulty of completely separating silver cyanide and silver cyanate, (c) the interference of other silver salts which may be precipitated.

The following method is found to give trustworthy and sufficiently accurate results in presence of any of the impurities which are usually associated with cyanides or cyanates. About 1 gram of the substance is distilled with a small excess of sulphuric or hydrochloric acid, and the carbon dioxide evolved absorbed in baryta solution, the barium carbonate formed being collected and titrated with *N*/10 hydrochloric acid. Any carbonate present is determined in a separate portion of the sample by precipitation in the cold with barium chloride. The reaction on which the method is based is $\text{HCNO} + \text{H}_2\text{O} = \text{CO}_2 + \text{NH}_3$. The ammonia remaining in the acid solution may be distilled off and estimated. This gives a check on the estimation of the carbon dioxide, and also shows whether there is any other nitrogenous substance present. Hydrogen cyanide passes over quantitatively with the carbon dioxide and may be titrated in the filtrate from the barium carbonate.

T. E.

Estimation of Formaldehyde and Paraformaldehyde. CLEMENS KLEBER (*Pharm. Review*, 1904, 22, 94).—To a concentrated solution of commercial sodium hydrogen sulphite, which usually contains a considerable quantity of free sulphurous acid, a solution of sodium hydroxide is added, until the odour of sulphur dioxide has disappeared. A slight excess of sodium hydroxide is immaterial. The solution is then diluted with water until 30 c.c. of it exactly neutralise 50 c.c. of *N* sodium hydroxide solution, using phenolphthalein as indicator. Towards this solution, formaldehyde and paraformaldehyde behave as alkalis and can be titrated accordingly. One c.c. of the solution corresponds with 0.05 gram of either formaldehyde or paraformaldehyde.

W. P. S.

Estimation of Aldehydes and Ketones in Essential Oils and Allied Substances. HERBERT E. BURGESS (*Analyst*, 1904, 29, 78—88).—The method to which particular attention is directed, and which gives trustworthy results with nearly all aldehydes and ketones generally met with, consists in heating the essential oil with a saturated solution of normal sodium sulphite, a soluble sulphonate being formed. The reaction, in the case of citral, is shown by the equation: $\text{C}_9\text{H}_{15}\cdot\text{CHO} + 2\text{Na}_2\text{SO}_3 + 2\text{H}_2\text{O} = \text{C}_9\text{H}_{17}(\text{NaSO}_3)_2\cdot\text{CH}(\text{OH})\cdot\text{SO}_3\text{Na} + 3\text{NaOH}$. With a ketonic substance, a similar reaction takes place.

Five c.c. of the oil are introduced into a 200 c.c. flask, having a neck graduated to 5 c.c. in divisions of 0.1 c.c., and a side tube reaching to the bottom of the flask for introducing the oil, reagent, &c. The sodium sulphite solution and a few drops of phenolphthalein solution are now added and the whole heated on a water-bath. The red coloration which appears is destroyed by the careful addition of dilute acetic acid (1:10) until, after the addition of a few more drops, no further colour is produced. The oil is then run up into the neck of the flask and its volume read off when cold. The difference between the reading and 5 c.c. gives the amount absorbed.

The method may be applied directly to many oils, but some, such as citron, lime, lemon, and orange oils, in which the amount of aldehyde is small, require to be previously concentrated. Results of experiments with a considerable number of essential oils are given in detail.

W. P. S.

Estimation of Certain Aldehydes and Ketones in Essential Oils. SAMUEL S. SADTLER (*J. Soc. Chem. Ind.*, 1904, 23, 303—305).—Several constituents of essential oils, notably citral, cinnamaldehyde, and carvone, may be estimated by titrating the sodium hydroxide liberated when the oils are treated with sodium sulphite solution. In the case of lemon oil, 10 grams of the sample are mixed with 10 c.c. of water and 4 drops of phenolphthalein solution and rendered just alkaline by the addition of $N/10$ potassium hydroxide solution. Twenty-five c.c. of a 20 per cent. sodium sulphite solution are added, an equal amount being measured out as a control. On agitation, a pink colour appears, and is discharged by the repeated addition of $N/2$ hydrochloric acid. When no more alkali is liberated, the mixture is heated on a water-bath and the neutralising continued. The control test is treated similarly. Both solutions are then titrated with $N/2$ sodium hydroxide solution until a pink coloration just reappears. The actual amount of hydrochloric acid used is then calculated into citral by considering that 1 molecule of citral is equivalent to 2 molecules of hydrochloric acid. The author provisionally suggests the equation for the aldehyde reaction as: $R \cdot CHO + 2Na_2SO_3 + 2H_2O = R \cdot CH(NaSO_3)_2 + 2NaOH + H_2O$, and for ketones, $R' \cdot CO \cdot R' + 2Na_2SO_3 + 2H_2O = CR'_2(NaSO_3)_2 + 2NaOH + H_2O$.

W. P. S.

Estimation of Sugar in Urine. J. M. A. HEGLAND (*Chem. Centr.*, 1904, i, 840; from *Pharm. Weekblad.*, 41, 133—137).—The urine is boiled with a definite volume of Fehling's solution and the excess of copper is estimated by titration with potassium ferrocyanide in the presence of acetic acid. This should be made of such a strength that it corresponds in copper-precipitating power with a 0.5 per cent. solution of dextrose.

L. DE K.

A Reaction of Urine with Resorcinol. RUDOLF ADLER and OSKAR ADLER (*Zeit. physiol. Chem.*, 1904, 41, 206—209).—The red colour produced by boiling with hydrochloric acid and resorcinol (Seliwanoff's reaction) is not necessarily due to lævulose. It often is

given by diabetic urine free from l  vulose, and sometimes by normal urine which has been kept. It is attributed to the presence of nitrites.
W. D. H.

Estimation of Sucrose, Lactose, &c., in Milks, &c. FREDERIC W. RICHARDSON and ADOLF JAFF   (*J. Soc. Chem. Ind.*, 1904, 23, 309—311).—Gravimetric methods, including the reduction of Fehling's and other metallic solutions, having failed to give trustworthy results, the authors rely on a polarimetric method. In the case of a mixture of sucrose and invert sugar, a reading of the solution is taken both at 20   and 86   and a reading of the inverted solution at 20  . Sucrose has $[\alpha]_D + 63.05^\circ$ at 86   instead of $+ 66.5^\circ$ at 20  , therefore any *plus* reading of the original solution at 86  , divided by 0.6305, gives the amount of sucrose. In 10 per cent. solution at 20  , the rotatory power of invert sugar is $- 20^\circ$. The same process is applied to solutions containing sucrose and lactose.

The acid mercury nitrate solution employed to precipitate the proteids of milk completely inverts sucrose when heated to 86  . It is therefore only necessary to take readings of the filtrate at 20   and 86   to estimate the sucrose and lactose. A solution of sucrose is also inverted by boiling with 2 per cent. of citric acid for 10 minutes, whilst lactose is entirely unaffected.

The authors are working out a method for solutions containing sucrose, lactose, and dextrose ("glucose"), based on the very different changes which the three sugars exhibit when heated in solutions containing 10 per cent. of hydrochloric acid.
W. P. S.

Estimation of Starch. WILLIAM A. NOYES, GILBERT CRAWFORD, CHARLES H. JUMPER, EDGAR L. FLORY, and ROBERT B. ARNOLD (*J. Amer. Chem. Soc.*, 1904, 26, 266—280).—See this vol., i, 373.

Action of Sodium Peroxide on Vegetable Fibres containing Lignin. A. DUSCHETSCHKIN (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 71—77).—The author gives the following general method for determining the proportion of cellulose in vegetable fibres containing lignin. From 0.5 to 2 grams of the fibre (1 part) are treated for $1\frac{1}{2}$ to 6 hours, according to the amount of lignin, with a solution prepared by dissolving 6 parts of magnesium sulphate in 100 of water and then adding 2 parts of sodium peroxide. For substances containing little lignin, such as sulphite cellulose, this treatment may be applied at once and need not be repeated. But when a large proportion of lignin is present, the fibre should be first of all boiled with a 1 per cent. sodium hydroxide solution and then treated twice or three times with the above oxidising mixture, with which it should be alternately boiled and heated on the water-bath. The freedom of the fibre from lignin may be tested by means of a solution of phloroglucinol in concentrated hydrochloric acid. If this treatment does not completely remove the lignin, the fibre may be subjected to the action of dilute potassium permanganate solution for 5—10 minutes and then treated on the filter with sodium hydrogen sulphite solution or very dilute sulphurous acid. The fibre,

after treatment with dilute acetic acid to dissolve the magnesium oxide remaining in it, is filtered off on to a hardened filter paper, washed several times with hot water, dried, and weighed. T. H. P.

Estimation of Acetic Acid in Acetate of Lime. ALBERT G. STILLWELL (*J. Soc. Chem. Ind.*, 1904, 23, 305—306).—The following method is described with the hope that a uniform method of analysis for this substance may be adopted. The sample is rapidly passed through a $\frac{1}{4}$ -inch sieve and the moisture estimated in it. An average sample is now passed through a 14-mesh sieve and the moisture again estimated. From this finely-divided sample, 2 grams are weighed out, placed in a round-bottomed flask of 300 c.c. capacity and having a neck 4 ins. long, 15 c.c. of syrupy phosphoric acid are added, and all drops carefully washed down from the neck with about 25 c.c. of water. The contents of the flask are then distilled and the distillate collected in an Erlenmeyer flask containing 30 c.c. of standard sodium hydroxide solution. Water is added to the distillation flask from time to time by means of a tapped funnel to keep the volume of liquid as near 40 c.c. as possible. After $1\frac{1}{4}$ hours, the distillate is neutralised by the further addition of standard sodium hydroxide solution, using phenolphthalein as indicator. The distillation is then carried on for 15 minutes longer, or until no more acid distils over. The sodium hydroxide solution used is of such strength that 1 c.c. corresponds with 0.0175 gram of acetic acid. W. P. S.

Estimation of Tartaric Acid. HERM. LEY (*Chem. Centr.*, 1904, i, 837; from *Pharm. Zeit.*, 49, 149).—Tartaric acid is dissolved in the smallest possible amount of water or alcohol, and a sufficiency of an alcoholic 5 per cent. solution of zinc acetate is added; when testing cream of tartar, water should be used instead of alcohol. After boiling for a minute, 100—150 c.c. of alcohol and 5 c.c. of 50 per cent. acetic acid are added, and after heating for 10 minutes on the water-bath, the zinc tartrate is collected, washed with alcohol, and ignited.

L. DE K.

Estimation of the Iodine Value of Oils by the Iodine-Bromide Method. LEONARD ARCHBUTT (*J. Soc. Chem. Ind.*, 1904, 23, 306).—Duplicate estimations by this method (*Abstr.*, 1902, ii, 112) were not found to agree as well as duplicates by the Wijs method, the difference being particularly marked in the case of oil of turpentine. The former method also gives lower results with other oils, especially those having high iodine values. W. P. S.

New Reactions for the Detection of Cocaine. C. REICHARD (*Chem. Zeit.*, 1904, 28, 299).—If to a concentrated solution of cocaine hydrochloride is added a strong solution of sodium nitroprusside, a characteristic, red, crystalline deposit of cocaine nitroprusside is obtained; morphine gives no precipitate. Uranium nitrate gives a yellow, crystalline precipitate, presumably a double cocaine-uranium compound. A solid particle of the hydrochloride, when moistened

with titanosulphuric acid, remains colourless, but on warming the acid turns a fine violet or blue.

If solid cocaine hydrochloride is rubbed with a little potassium ethyl sulphate and then moistened with a little sulphuric acid, no effect is observed, but on warming a peppermint-like odour is noticed; this reaction is very characteristic and delicate. When the hydrochloride is rubbed with urea and then moistened with sulphuric acid, no change takes place in the cold, but on warming a gradually increasing blue coloration is observed; ethylenediamine hydrochloride may be substituted for urea, but hydroxylamine produces no effect.

L. DE K.

Creatinine and Creatine in Urine. OTTO FOLIN (*Zeit. physiol. Chem.*, 1904, 41, 223—242).—Creatinine may be estimated by a colorimetric method, based on Jaffé's reaction (Abstr., 1886, 1056). A colorimeter which is provided with two tubes and can be read to 0.1 mm. is employed, also 0.5*N* potassium dichromate solution, a nearly saturated (1.2 per cent.) picric acid solution, and 10 per cent. sodium hydroxide solution. Exactly 8 mm. of the dichromate solution are placed in the one tube, 10 c.c. of urine are placed in a 500 c.c. flask, 15 c.c. of picric acid solution and 5 c.c. of the alkali added, the whole shaken several times, left for a few minutes, and then made up to the mark with water. This solution is placed in the second tube, and the length of solution required to give the same colorimetric effect as the 8 mm. of dichromate determined. The mean of several determinations is taken and then if this value = x , $8.1 \times 10/x$ = mg. of creatinine in 10 c.c. of urine. If $x < 5$, then only 5 c.c. of urine should be used; for the original solution of $x > 13$, then 20 c.c. of urine should be taken.

The presence of creatine in certain urines has been established by determining the amount of creatinine originally present by the above method, then heating 10 c.c. of the urine with 5 c.c. of *N*-hydrochloric acid for 3 hours on the water-bath, and again determining the amount of creatinine. Any increase in the amount is due to the conversion of creatine into creatinine under the influence of the hydrochloric acid. Some urines are quite free from creatine, others contain minute amounts, and others large quantities.

Details are given for the preparation of pure creatinine from urine.

In the estimation of nitrogen in creatinine by the Kjeldahl method, the best results are obtained when the substance is mixed with concentrated sulphuric acid (20 c.c.), 2 grams of a mixture of copper sulphate (10 per cent.) and potassium sulphate (90 per cent.), 5 grams of water, and 5 grams of crystallised disodium phosphate.

The decomposition is regarded as a process of hydrolysis, hence the need for water, but not for permanganate (compare Malfatti, Abstr., 1903, ii, 754).
J. J. S.

Colour Reactions of Morphine and Codeine. EMILIO GABUTTI (*L'Orosi*, 1903, 26, 1—2).—Formaldehyde gives the same colour reaction with either morphine or codeine in sulphuric acid solution, but

when heated with chloral or bromal, morphine gives a violet coloration and codeine an azure-green in presence of sulphuric acid. If the codeine contains morphine, the azure-green colour becomes brownish-violet. The best method of observing this reaction is to gradually heat and stir well the codeine or morphine with concentrated sulphuric acid in a porcelain basin until a faint red coloration appears and then to add a small quantity of chloral or bromal and continue stirring.

The azure-green liquid obtained with codeine gradually changes its colour to red; this red coloration is also obtained by the addition of a few drops of water or alkali hydroxide.

Dionine (ethylmorphine) exhibits similar behaviour to codeine, whilst eroine (diacetylmorphine) yields a brownish-red coloration.

The other alkaloids of the *Papaveraceæ* such as papaverine, narcotine, thebaine, meconine, &c., do not yield these colour reactions.

T. H. P.

Toxicological Researches on Morphine. MARUSSIA BAKUNIN and VINCENZO PETITTI (*Gazzetta*, 1904, 34, i, 1—38).—The early part of the paper reviews the work of other investigators in estimating or detecting morphine in the animal organism. Experiments are described in which the quantity of morphine present in the various organs of rabbits which had been killed by injecting the alkaloid (0·8 gram per kilo. of body-weight) was estimated. Different methods of estimation give different results; thus the total amount of morphine in all the organs of two rabbits of equal weight, killed by the injection of 1·2 grams of the alkaloid, was found by Dragendorff's method to be 0·2647 gram and by the Stass-Otto method to be 0·0784 gram; the organs of a larger rabbit into which 1·70 grams had been injected were found by Senkowski's method to contain only 0·0730 gram of morphine. As regards the separate organs, the stomach contains invariably the largest proportion of the alkaloid, followed by the bladder and urine and the large intestine; in the liver, kidneys, brain, heart and spleen, and lungs the amount of morphine present is small, whilst traces only are found in the muscles, brain, and salivary glands.

After a month's putrefaction practically the same amount of morphine is found in the body of a rabbit as immediately after death, but after two months there is a decrease in the quantity of from 20—40 per cent.

The principal result established seems to be the fact that only a small proportion, namely, 5—20 per cent., of the morphine injected can be accounted for; whether this is due to the methods of estimation employed being unsatisfactory or to a modification of the morphine within the organism remains still to be decided.

W. A. D.

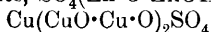
General and Physical Chemistry.

Spectrum of Zinc. MAURICE HAMY (*Compt. rend.*, 1904, 138, 959—961).—Taking the red ray $\lambda 508$ of the cadmium spectrum as a line of reference, the author has measured the wave-lengths of the rays of the zinc spectrum, using the interference method (compare Fabry, this vol., ii, 305), and the results agree so closely with those obtained by Perot and Fabry (*J. Physique*, 1900) that the accuracy of the method is fully established. M. A. W.

[Influence of Temperature on the Specific Rotatory Power of Strongly Optically Active Compounds.] HERMANN GROSSMANN (*Ber.*, 1904, 37, 1260—1261).—The author in a recent paper (this vol., i, 153) overlooked the results obtained by Frankland and Wharton (*Trans.*, 1896, 69, 1583). W. A. D.

Recent Researches on Radioactivity. PIERRE CURIE (*J. Chim. Phys.*, 1903, i, 409—449).—The paper contains an excellent summary of the chief work that has been done on radium and radioactivity and has a full bibliography appended. There is necessarily little new in the paper, but the interesting fact of the explosion of a sample of radium chloride on heating is recorded, and the author urges some weighty objections to the orthodox view of the gaseous nature of the emanation. L. M. J.

Application of Blondlot's Rays to Chemistry. ALBERT COLSON (*Compt. rend.*, 1904, 138, 902—904).—When a solution of potassium hydroxide is added to a solution of zinc sulphate, n_1 rays are emitted, and can be detected by the diminution in the brightness of phosphorescent sulphide placed near the tube; the rays disappear before sufficient alkali has been added to completely precipitate the zinc hydroxide, and do not reappear on the further addition of alkali. If, however, the order of the experiment is reversed, and the zinc sulphate solution be added to the potassium hydroxide solution, there is no action on the phosphorescent sulphide, even if a large excess of the metallic salt be added. Similar results are obtained when copper sulphate is used instead of zinc sulphate. The emission of the Blondlot rays is due to the formation of basic salts, $\text{SO}_4(\text{Zn}\cdot\text{O}\cdot\text{ZnOH})_2$ and



respectively, when the alkali is added to the solution of the metallic salt, and the molecular condensation produces effects analogous to those obtained by mechanical compression (compare Blondlot, *Compt. rend.*, 1903, 137, 962). M. A. W.

Origin of the Blondlot Rays disengaged during Chemical Reactions. ALBERT COLSON (*Compt. rend.*, 1904, 138, 1098—1099. Compare preceding abstract).—The chemical actions which emit Blondlot rays are always accompanied by physical changes such as contraction,

cooling, &c., which act in the same sense ; thus the crystallisation of a supersaturated sodium sulphate solution emits n_1 rays, probably due to the contraction that accompanies the change. Again, when chrome alum dissolves in cold water to form a violet solution, n rays are emitted, but if it dissolves rapidly in boiling water to form a green solution n_1 rays are emitted ; in the first case there is an absorption of heat, and in the second there is a chemical change (2 mols. of the alum losing 1 mol. of H_2SO_4), also accompanied by an absorption of heat, and the rapid cooling produced by these two physical actions is probably the cause of the n_1 rays.

M. A. W.

Disruptive Discharge in Air at Normal Pressures and the Action of Radium on it. D. M. SOKOLZOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, ii, 25—38).—The author's experiments lead to the following conclusions : (1) of the two electric emissions taking place in a disruptive discharge in air at normal pressure, the positive is the essential one. The evidence for this is as follows : the spark jumps to a greater distance from a positive point than from a negative one ; when the two electrodes are similar, connection of the anode to earth diminishes the spark, whilst earthing the cathode increases the intensity of the spark ; the electric emission from the anode is more intense than that from the cathode and more readily produces a spark ; observation of the transformation of a slow discharge into a spark shows that the latter passes from the anode to the cathode ; several other published facts indicate the dominant rôle of the anode in the formation of a spark, especially the action of a magnetic field, the pressure and fall of potential in the spark, the incandescence of the cathode, and the analogy with the discharge in Geissler tubes. (2) Radium paralyses the positive emission, but has no appreciable action on the negative one ; the action of the radium becomes less as the electrode approaches a point in form. (3) If large oscillations are absent from the spark circuit, radium extinguishes a moderately large spark, and this is done the more readily the larger the superficial area of the anode. (4) On an oscillating spark, radium exercises a peculiar action ; with a positive point and a negative disc, radium will extinguish a spark if near to it, but will brighten a spark some distance off ; all other oscillating sparks are considerably intensified.

T. H. P.

Influence of Temperature on Electrical Conductivity of Potassium. ARCIERO BERNINI (*Nuovo Cimento*, 1903, [v], 6, 289—297).—The author's measurements of the electrical conductivity of potassium show that this metal is one of the best conductors. Its conductivity diminishes proportionately as the temperature rises. The temperature-coefficient is greater for the liquid than for the solid state, and the variation of the resistance on change of state (at 62.04°) takes place very suddenly, the increase being in the ratio of 1.392 to 1.

T. H. P.

Conductivity of Saturated Aqueous Solutions of Black and Red Mercuric Sulphides. RALPH G. VAN NAME (*Zeit. anorg. Chem.*, 1904, 39, 108—111).—The conductivity of aqueous solutions of black

and red mercuric sulphides was determined. The measurements in the case of the black sulphide were influenced by the fact that the solid itself is a conductor, and it was impossible to avoid the presence of small amounts of it in the liquid between the electrodes; the conductivity of the solid red form, on the other hand, is very slight. The values obtained are quoted. For both sulphides, $K_{25} = 0.01$ to 0.02×10^{-6} .
A. McK.

Formation of Complex Ions. HANS EULER (*Ber.*, 1904, 37, 1704—1714. Compare Abstr., 1903, ii, 544, 717; this vol., ii, 11).—From the *E.M.F.* of concentration cells, metal | metallic thiosulphate + sodium thiosulphate | metallic chloride or sulphate | metal, the values of K are calculated for the complex ions. $\text{TiNa}(\text{S}_2\text{O}_3)_2$, $K = 7 \times 10^{-4} - 9 \times 10^{-4}$; $\text{CdNa}_2(\text{S}_2\text{O}_3)_4$, $K = 3.5 \times 10^{-8} - 5 \times 10^{-8}$; $\text{PbNa}_2(\text{S}_2\text{O}_3)_4$, $K = 3.5 \times 10^{-8} - 8 \times 10^{-8}$. Zinc, nickel, and ferrous thiosulphates form few or no complex ions with sodium thiosulphate. The dissociation constants are as follows: Ag, $K = 10^{-13}$; Cd, $\sqrt{K} = 2 \times 10^{-4}$; Pb, $\sqrt{K} = 2.5 \times 10^{-4}$; Tl, $K = 8 \times 10^{-4}$; Ni, $\sqrt{K} = > 10^{-1}$; Fe, $\sqrt{K} = > 10^{-1}$; Zn, $\sqrt{K} = > 0.5$.

As carbamide does not form complex ions with silver salts, Rosenheim and Loewenstamm's complex cathions are regarded as sulphur, not as nitrogen, combinations (Abstr., 1903, i, 325). The author discusses the cause of the formation of complex ions.
G. Y.

Relation between the Solution Pressure and the Heat of Ionisation of Metals. ARTHUR KORN and EDUARD STRAUSS (*Festschr. Ludwig Boltzmann*, 1904, 277—281).—The authors suppose that forces of repulsion between the particles of a metal are opposed by electrostatic forces acting between positively and negatively charged groups. The immersion of the metal in a solvent with high dielectric constant favours the forces of repulsion, and metallic particles pass into solution until the osmotic pressure reaches the value defined by the electrolytic solution pressure. From these assumptions, the authors draw the conclusion that the order of magnitude of the electrolytic solution pressures of the metals must coincide with the order of the values of the expression $Q + \alpha^2 n^2 m^2$, where Q is the heat of ionisation, n the valency, and m the atomic weight of the metal in question, whilst α^2 is a constant. Using Ostwald's data for Q (Abstr., 1893, ii, 357) and taking $\alpha = 1/30$, the authors show that this conclusion is verified for the series Mg, Zn, Cd, Fe'', Tl, Co, Ni, Cu'', Hg', Ag. Lead, however, does not fall into its proper place between Ni and Cu.
J. C. P.

Decomposition Curves of Lithium Chloride in Alcohols and the Electro-deposition of Lithium. HARRISON E. PATTEN and WM. ROY MOTT (*J. Physical Chem.*, 1904, 8, 153—195).—The electrolysis of solutions of lithium chloride in the following alcohols was studied: ethyl, propyl, butyl, amyl, and allyl alcohols, glycerol, and phenol. The solubility at 25° of the salt in these compounds in the order named is 2.475 per cent., 3.72 per cent., 9.56 per cent., 8.26 per cent.
27—2

cent., 4.20 per cent., 4.14 per cent., and 1.89 per cent. Aqueous solutions were first examined, and tables and curves are given showing the anode and cathode polarisation for various currents. In the alcohols there are three stages in the electrolysis: (1) that of the residual current where the dissolved gases depolarise the electrodes, (2) the formation of lithium alkyloxides, (3) deposition of lithium. In ethyl alcohol, no deposit of lithium was found until a very high current density (500 amperes per square foot) was reached, this being obtained by the use of a platinum wire as cathode. The metal appeared from solutions in propyl alcohol at a current density of about one-tenth that required for ethyl alcohol. In solutions in butyl alcohol, however, the deposition of lithium was readily obtained, the current density required being only about one-twentieth of that used in electrolytic copper refining. In amyl alcohol also, the lithium was deposited in considerable quantity, but in allyl alcohol and glycerol separation of lithium was not obtained. The authors discuss the conditions necessary for the electro-deposition of an alkali metal. It is evident that the rate of liberation must be greater than the rate of reaction between metal and solvent, and hence a solvent of slow action is essential. It must, however, possess also moderate solvent action and yield a fairly conducting solution in order that the necessary current density may be obtained. The single potential of lithium calculated from the polarisation values as well as from thermal data is 2.41 volts.

L. M. J.

Electric Osmose in Methyl Alcohol. A. BAUDOUIN (*Compt. rend.*, 1904, 138, 898—900).—Using Perrin's apparatus (compare Perrin, *Compt. rend.*, 1903, 136, 1388, 1441), the author has shown that although the electric osmose in methyl alcohol is proportional to the difference of potential on the two sides of the porous septum, it requires a difference of potential of 250—300 volts in order to produce an effect comparable with that obtained by 60—100 volts in the case of water. The sign of the electric osmose varies with the nature of the porous septum, being in the contrary direction to the current in the case of chromium chloride, lead sulphate, or manganese dioxide, and in the same direction as the current in the case of silica, arsenic trisulphide, sulphur, or lead iodide. The addition of traces of an electrolyte diminishes the electric osmose or reverses its sign, whilst non-electrolytes, such as benzene, naphthalene, menthol, or camphor, have no effect. Finally, just as the addition of potassium hydroxide to water causes a positively charged septum to become negative, that is, reverses the sign of the electric osmose, so a septum of chromium chloride which is positively charged in contact with absolute methyl alcohol becomes negatively charged in a *N*/1500 solution of potassium methoxide. The analogous behaviour of acids is not so readily shown in the case of methyl alcohol owing to the esterification of the alcohol, but if added in sufficient quantity the sign of the osmose is reversed (compare Perrin, this vol., ii, 8).

M. A. W.

Electric Resistance Thermometry at the Temperature of Boiling Hydrogen. JAMES DEWAR (*Proc. Roy. Soc.*, 1904, 73, 244—251. Compare Abstr., 1901, ii, 308).—The following metals

and alloys have been used in the experiments: platinum, gold, silver, copper, palladium, iron, nickel, platinum-rhodium, and German silver. It appears that the resistance of a pure metal diminishes regularly with temperature, approaching asymptotically to a definite value. Thus the parabolic connection between temperature and resistance is no longer valid at such low temperatures as the boiling point of hydrogen. Further evidence of this abnormal behaviour at low temperatures is found in the exceptionally high value (2.5) of the platinum thermometer constant δ , based on the resistances at 100° , 0° , and -182.5° (compare the usual value $\delta = 1.5$, based on the resistances at 444.5° , 100° , and 0°).

J. C. P.

Influence of the Change of Specific Heat on the Work done in a Transition. JACOBUS H. VAN't HOFF (*Festschr. Ludwig Boltzmann*, 1904, 233—241).—When the change of specific heat accompanying a transition is taken into account (see Richards, *Proc. Amer. Acad.*, 1902, 293), the influence of temperature on the work done in the transition may be expressed by the following equation: $E = E_0 + AT - ST \log T$, where E is the free energy at the temperature T , E_0 that at absolute zero, S is the difference of the specific heats of the system before and after transition, A is an integration constant. From the above, it follows that $dE/dT = A - S(1 + \log T)$, and where the change or transition takes place without alteration of concentration, as in the case $\text{Mg} + \text{ZnSO}_4, \text{aq} = \text{Zn} + \text{MgSO}_4, \text{aq}$, $dE/dT = -S(1 + \log T)$. For 18° , this leads to $dE/dT = -6.7S$, and the author shows that this relationship is approximately fulfilled in a number of cases.

In the change of liquid \rightarrow solid, or in other transitions which take place at a definite temperature, A cannot be neglected, but further consideration of the equations shows that for the possibility of a transition of any kind S must be >0 , that is, the form which is stable at higher temperatures must have the greater specific heat. This is known to be the case for every change liquid \rightarrow solid and for the majority of transition changes among elements or compounds exhibiting polymorphism. The exceptions among the latter may be due to incorrect determinations of the specific heats.

The equation given above permits also the general conclusions that at low temperatures those systems are stable the formation of which is accompanied by development of heat, whilst at high temperatures only those heat-absorbing reactions will take place which yield products with higher specific heat.

J. C. P.

Specific Heats of Metals and the Relation of Specific Heat to Atomic Weight. III. WILLIAM A. TILDEN (*Proc. Roy. Soc.*, 1904, 73, 226—227. Compare Abstr., 1900, ii, 524; 1903, ii, 265).—The specific heats of the tellurides of tin, silver, and nickel, of two alloys of silver and aluminium, and of the elements involved in these have been determined over a wide range of temperature, amounting in most cases to about 700° . The molecular heat of each compound at successive temperatures is found to differ but slightly from the sum of the atomic heats of the component elements, and Neumann's law is therefore approximately true at all temperatures. It appears also

that the specific heat of a solid is determined by the nature of the atoms composing the physical molecules, and is not a measure of the thermal work done in expansion. J. C. P.

Determination of the Heat of Combustion with the Calorimetric Bomb by Berthelot's Method. PAWEŁ ZUBOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 275—287).—The author discusses such questions as the necessity for the extreme purity of a substance, its freedom from isomerides, &c., the heat of combustion of which is to be determined, and, when liquids are investigated, the difficulty of preventing evaporation in the calorimetric bomb, &c. T. H. P.

Thermochemical Studies. DANIEL LAGERLÖF (*J. pr. Chem.*, 1904, [ii], 69, 273—309).—A criticism of Thomsen's theory of the heat of formation of carbon compounds. G. Y.

Calculation of the Heats of Combustion of Organic Compounds containing Nitrogen. PAUL LEMOULT (*Compt. rend.*, 1904, 138, 900—902. Compare Abstr., 1903, ii, 410; this vol., ii, 12).—By assigning to the group $\cdot\text{C}\cdot\text{N}$ the thermal value 16.5 Cal. and subtracting from it 10 Cal. for each group $\cdot\text{N}\cdot\text{H}$, the molecular heat of formation of the compound $\text{C}_x\text{H}_y - a\text{NmHaOp}$ is given by the expression $102x + 55/2y + 16.5m - 10a - \Sigma p\phi$; ϕ having the value 55 Cal. for amides, imides, &c.

The molecular heats of combustion of a number of amines, amides, imides, nitriles, and compounds with nitrogen in the ring, calculated by means of the above formula, are given in the paper, and shown to agree closely with the experimental values. M. A. W.

Cyclic Amines. PAUL LEMOULT (*Compt. rend.*, 1904, 138, 1037—1039).—The discrepancy between the experimental value for the heat of combustion of some amines and the value calculated from the formula (compare this vol., ii, 12 and preceding abstract), although negligible in the case of the secondary and tertiary amines, amounts to 22.6 Cal. in the case of some primary amines, and is probably to be attributed to some error in the experimental determination, for the author has determined the heats of combustion of xylydine [4-amino-1:3-xylene], ethylaniline, anisidine, and α - and β -naphthylamines, and finds that the experimental values agree very closely with those calculated by means of his formula. The molecular heat of combustion at constant volume of xylydine is 1111.42 Cal.; of ethylaniline, 1125.6 Cal.; of anisidine, 927.29 Cal.; of α -naphthylamine, 1268.78 Cal.; of β -naphthylamine, 1266.5 Cal. M. A. W.

Free Energy of Formation in Several Reactions of Technical Importance. HANNS VON JÜPTNER (*Zeit. anorg. Chem.*, 1904, 39, 49—68).—The author discusses the alteration of the free energy of a reaction with the temperature and brings forward an interpolation formula on the assumption that the alteration of free energy is a linear function of the absolute temperature, an assumption which could only be strictly correct if specific heats of substances were inde

pendent of temperature. The free energy of formation of steam, of carbon dioxide from carbon monoxide and oxygen, of carbon monoxide from amorphous carbon and oxygen, of carbon dioxide from amorphous carbon and oxygen, and of carbon monoxide from carbon and carbon dioxide are calculated.

A. McK.

Determination of Melting Points. LÉON MAQUENNE (*Bull. Soc. chim.*, 1904, 31, 471—474).—The author states that Muther and Tollens' statement (this vol., i, 224) that in the determination of the melting point of hydrazones Maquenne's metal block process (*Bull. Soc. chim.*, 1887, 48, 771) presents no advantage over the capillary tube method is only true when the block is slowly heated. In using the block, it should be rapidly heated and small portions (0.1 mg.) of the substance should be projected on to it. When the temperature is such that the substance melts instantaneously, this should be taken as the melting point. Under these conditions, phenylglucosazone melts instantaneously at 306° and leucine at 340°. These melting points are very different from those recorded for capillary tube determinations, in which case the melting point varies with the rate of heating.

T. A. H.

Freezing Points of Solutions as Steady Temperatures. K. PRYTZ (*Zeit. physikal. Chem.*, 1904, 47, 729—732. Compare Abstr., 1902, ii, 382).—An apparatus constructed on the lines already laid down (*loc. cit.*) is sketched, and the procedure to be adopted in using it is described in detail. The apparatus has been used successfully not only with aqueous, but also with benzene, solutions.

J. C. P.

Course of the Decrease of Vapour Tension for Aqueous Solutions. ANDREAS SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 6, 628—641).—The molecular rise of the boiling point for solutions of sodium chloride and potassium chloride respectively had been previously found by the author to have a minimum value at ± 0.3 gram-mol., whilst with various nitrates examined, the molecular rise of the boiling point decreased continually with increase of concentration. The diminution of the vapour tension of solutions of sodium chloride and nitrate respectively has now been determined by means of the micro-manometer, where the aniline-water manometer was replaced by Lord Rayleigh's manometer (Abstr., 1901, ii, 542). The results obtained by both these manometers are concordant, and are contrasted with those obtained by Raoult and others by cryoscopic methods.

Solutions of sodium nitrate, which behave qualitatively in a normal manner, do not follow Ostwald's dilution law, whereas solutions of potassium nitrate do.

A. McK.

High Temperature Gas Burner. LUDWIG HORMUTH (*Zeit. anal. Chem.*, 1904, 43, 231).—By adding to an ordinary Bunsen burner an enlarged chamber for the admixture of the gas and air, the temperature of a blowpipe flame can be attained.

M. J. S.

Ring Burner. LUDWIG HORMUTH (*Zeit. anal. Chem.*, 1904, 43, 231—232).—This is a ring-shaped tube with orifices within the ring. It can be attached to an ordinary Bunsen burner and then forms a support for the vessels which are to be heated. M. J. S.

Apparatus for Regulating the Pressure when Distilling under Reduced Pressure. JAN RUTTEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 6, 665—668).—An apparatus for regulating the pressure during vacuum distillation is illustrated and described.

A. McK.

Volume of Atoms and Molecules. ISIDOR TRAUBE (*Festschr. Ludwig Boltzmann*, 1904, 430—440).—A summary of the author's previous papers on this subject. J. C. P.

Atomic Volumes of the Rare Earths and their Significance for the Periodic Classification. CARL BENEDICKS (*Zeit. anorg. Chem.*, 1904, 39, 41—48).—The rare earths from lanthanum to ytterbium are brought together by the author into one grouping in the vertical rows III and IV of Mendeléeff's periodic classification; they are accordingly placed between barium and tantalum.

A. McK.

Metric Standard of Volume. THEODORE W. RICHARDS (*J. Amer. Chem. Soc.*, 1904, 26, 413—414).—A plea for the adoption of the millilitre as the standard of volume instead of the cubic centimetre, the former designation being more exact and less cumbrous than the latter.

E. G.

New Pycnometer. S. BOŠNJAKOVIĆ (*Zeit. anal. Chem.*, 1904, 43, 230).—The thermometer which forms the stopper of the flask has a narrow tube fused into its stem parallel with the scale, and opening below into the flask, whilst terminating above in a small, stoppered funnel.

M. J. S.

A New Pycnometer Pipette. E. FISCHER (*Chem. Zeit.*, 1904, 28, 359).—The author describes a pycnometer pipette which he has found convenient when small quantities of liquid are dealt with.

A. McK.

New Method of Determining Compressibility with Application to Bromine, Iodine, Chloroform, Bromoform, Carbon Tetrachloride, Phosphorus, Water, and Glass. THEODORE W. RICHARDS and WILFRED NEWSOME STULL (*J. Amer. Chem. Soc.*, 1904, 26, 399—412).—Methods of determining compressibility are described, which are applicable to nearly all substances. Two forms of apparatus have been devised, one for solids and the other for liquids. The first form consists of a short, wide, glass test-tube fitted with a well-ground, hollow stopper, which terminates above in a slender funnel tube provided with a platinum wire projecting downwards. The tube is filled with mercury, and the change in volume for different pressures is

measured by placing it under the liquid in the barrel of a Cailletet compression apparatus, adding successive weighed portions of mercury, and noting on each occasion the pressure required to make and break the electrical contact between the platinum wire and the mercury. The substance, the compressibility of which is to be determined, is introduced beneath the mercury, and the experiment is repeated. The differences observed between the results of the two series of experiments represent the differences between the compression of the substance and that of an equal volume of mercury. Solids which attack mercury are surrounded with water, whilst liquids which attack mercury are enclosed in thin, flat, flexible glass bulbs. The decrease in volume of these bulbs on compression is determined as if they were homogeneous solids, and a correction is made for the change in volume of the mercury and glass.

In the apparatus employed for liquids which do not attack mercury, the funnel tube is replaced by a doubly-bent glass tube which contains the mercury necessary for making electrical contact. For details of these methods and the precautions to be observed in carrying out the experiments, the original must be consulted.

The compressibility of bromine, iodine, chloroform, carbon tetrachloride, bromoform, phosphorus, and water was determined by reference to mercury in most cases up to 500 or 600 atmospheres, and from the results were also obtained the value for glass and a qualitative indication of the compressibility of liquid chlorine; in each case, the temperature was maintained at 20°.

The "megabar," the pressure of a megadyne per sq. cm., is recommended as the most convenient unit of pressure; it is equal to 0.987 atmosphere. Expressing the pressures in terms of this unit, the average compressibilities, $\frac{\Delta V/V}{\Delta p}$, of the various substances between 100 and 200 atmospheres, compared with regard to their relative decrease with increasing pressure, are found to be as follows: iodine, 0.000013; bromine, 0.0000574; liquid chlorine, 0.00011; carbon tetrachloride, 0.0000883; chloroform, 0.0000881; bromoform, 0.0000467; water, 0.0000441; phosphorus, 0.0000208; glass, 0.00000231; mercury, 0.00000382 (Amagat).

Approximate determinations were made of the heat of compression of water and mercury, and a manometric method, based on the difference between the compressibility of water and mercury, is proposed for calibrating high pressure gauges. E. G.

[Law of the Rectilinear Diameter.] ALEXIUS BATSHINSKI (*Zeit. physikal. Chem.*, 1904, 47, 743—744. Compare Abstr., 1903, ii, 10).—A reply to Bakker (this vol., ii, 310). J. C. P.

Contributions to the Knowledge of van der Waals' ψ -Surface. VIII. The ψ -Surface in the Neighbourhood of a Binary Mixture, which behaves as a Pure Substance. JULES E. VERSCHAFFELT (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 6, 649—658).—A theoretical paper, which does not admit of being adequately abstracted. A. McK.

The Liquid State and the Equation of State. JOHANNES W. VAN DER WAALS (*Arch. Neer.*, 1904, 9, ii, 1—33).—The van der Waals equation, although qualitatively valuable, does not furnish results which are numerically exact. The author therefore discusses the question whether the constants a and b should not be regarded as temperature or pressure variables. Clausius had suggested that a should be replaced by $a.273/T$. The author raises objections to this, and considers that a is probably constant, but that b diminishes with the volume. Thus, for carbon dioxide the value of b has been found to be 0.00242 in the gaseous state, but 0.001565 in the liquid state; and he advances theoretical considerations which show that b must be regarded as a variable. The diminution in b may be regarded as due to a real decrease in the volume of the molecules themselves or to a variation of the relation existing between b and this volume. The equations relative to the vapour tension and compressibility are then considered.
L. M. J.

Distribution of a Non-dissociating Substance between Two Solvents. G. JAGER (*Festschr. Ludwig Boltzmann*, 1904, 313—315).—A proof (based on the kinetic theory) of Nernst's proposition that the ratio of the concentrations of a non-dissociating substance in two immiscible solvents is independent of the absolute quantity of the substance dissolved.
J. C. P.

Nature of Concentrated Solutions of Electrolytes. Hydrates in Solution. HARRY C. JONES and FREDERICK H. GETMAN (*Amer. Chem. J.*, 1904, 31, 303—359).—The experiments described in this paper are a continuation of work previously recorded (*Abstr.*, 1902, ii, 489; 1904, ii, 235). The freezing points, conductivity, and refractivity of solutions of the chlorides, sulphates, and nitrates of manganese, nickel, cobalt, copper, and aluminium have been determined. All these substances, except aluminium sulphate, in which case the proper dilution was not employed, showed a minimum value in the molecular depression of the freezing point. No sign of a minimum was exhibited by the conductivity and refractivity curves. Determinations have also been made of the molecular elevation of the boiling point produced by potassium iodide, sodium iodide, cadmium iodide, ammonium iodide, and sodium bromide. With the exception of sodium bromide, all these salts show a well-defined minimum in the molecular elevation, but this occurs at greater concentrations than the minimum in the corresponding freezing point curves.

It was suggested by Jones and Chambers (*Abstr.*, 1900, ii, 262) that these phenomena may be explained by the theory that in concentrated solutions the dissolved substance combines with the solvent with formation of hydrates, which exist in the solution together with a small proportion of ions resulting from the electrolytic dissociation of the salt, and that those substances which yield crystals containing the largest amount of water of crystallisation would be expected to form the most complex hydrates in solution. The results obtained in the present investigation afford strong evidence that this interpretation is correct. The composition of the

hydrates was calculated in those cases in which sufficient data had been obtained, and it was found that the hydrates decrease regularly in complexity with the dilution and disappear entirely at a dilution greater than that at which the freezing point minimum occurs.

E. G.

Effect of One Associated Solvent on the Association of Another Associated Solvent. HARRY C. JONES [and GRANTLAND MURRAY] (*Festschr. Ludwig Boltzmann*, 1904, 105—112).—The solvents studied were water, formic and acetic acids. The molecular weights of these three substances when dissolved up to fairly high concentrations in each of the other two have been determined by the freezing point method, and it is found that the association of the solute is in each case less than that of the same substance in the pure state. In other words, one associated liquid diminishes the association of another associated liquid, a result that has a direct bearing on Jones and Lindsay's observation that certain salts conduct better in pure methyl alcohol solution than in aqueous methyl alcohol solution (see Abstr., 1903, ii, 55).

J. C. P.

Polymerisation of Organic Compounds in the Solid State. GEORGE G. LONGINESCU (*J. Chim. phys.*, 1903, i, 296—301).—The formula $(T/CD)^2 = n$, where T is the absolute melting point, D the density in the solid state, C a constant, and N the number of atoms in the molecule, is examined (compare Abstr., 1903, ii, 531; this vol., ii, 112), to see whether it is valid for solids as for liquids. For $C = 70$, a large number (66) of compounds such as citric acid, phthalic acid, aniline, nitrobenzene, &c., gave results approximately normal. Some (20), including acetic acid, formic acid, benzene, phenol, carbamide, &c., gave high values for n , indicating polymerisation. A number of compounds, however (16), gave low values for n ; these include benzoic acid, azobenzene, glucose, and mannitol, although in the liquid state they give normal values. This would indicate dissociation, but the author considers that it is more probable that the value of C should be fixed at 50. The latter compounds would then be normal, but the majority of the compounds (those of the first set) would appear to be slightly polymerised. Further investigations are promised.

L. M. J.

Polymerisation and Dissociating Power of Oximes. PAUL DUTOIT and ARTHUR FATH (*J. Chim. phys.*, 1903, i, 358—378).—The work of Ramsay, Guye, Beckmann, and others has indicated that, in general, the following classes of compounds are more or less polymerised in the liquid state: alcohols, phenols, aliphatic acids, aldehydes, nitriles, ketones, amines, urethanes, and thiocarbimides. Associated liquids are further generally characterised by a high latent heat of vaporisation, low surface tension and vapour pressure, whilst mixtures of associated liquids do not generally obey the simple mixture laws. They are also usually good solvents, and possess dissociative power (Abstr., 1897, ii, 546). The authors have therefore examined the relations between the polymerisation and dissociative power for a number of oximes, the following being employed: aldoxime,

propaldoxime, isovaleraldoxime, cœnanthaldoxime, acetoxime, methylpropylketoxime, and mesityl oxide oxime, and for these the paper contains the values obtained for capillarity, molecular refraction, densities at various temperatures, and viscosity. The surface tension for all these compounds indicates polymerisation, but the authors do not consider that quantitative measures of the association are given, especially as some of the compounds consisted of mixtures of the *syn*- and *anti*- varieties, the equilibrium of which may vary with temperature. Cryoscopic observations in benzene solution were also made, and in the case of acetoxime, methylpropylketoxime, and isovaleraldoxime association was indicated, although in acetic acid solution the two former compounds yielded normal values. In regard to their association, the oximes appear to occupy a place intermediate between the alcohols and acids on the one side, and the less abnormal liquids, as nitriles and aldehydes, on the other. The results of the work on the solvent and dissociative power are reserved for a later paper.

L. M. J.

Surface Tension and Molecular Complexity of Active Homologous Compounds. MISS IDA HOMFRAY and PHILIPPE A. GUYE (*J. Chim. phys.*, 1904, i, 505—544).—A number of homologous series of optically active esters exhibit a maximum in the specific rotation; the molecular rotation in some of these series converges to a limiting constant value, in others this constant also passes through a maximum. This has been regarded by some chemists as due to the molecular disymmetry itself passing through a corresponding maximum, whilst by others it has been considered as due to the fact that the first members of the series in question are characterised by polymerisation or partial association (Frankland, *Trans.*, 1899, 347). The authors have therefore investigated the polymerisation in those series which exhibit a maximum in the molecular rotation, employing the method of Ramsay and Shields. The results do not indicate association in any of the compounds examined, as the molecular surface energy was in almost all cases normal; the maximum is therefore not due to association. Some values for the constant were obtained which are higher than any previously found, reaching to above 3·6. The authors hence agree with Dutoit and Friderich that the value of K cannot be regarded as constant for all liquids, and that the linear nature of the temperature curve of the molecular surface energy is a better indication of normality. The higher values of K may be either due to the fact that the molecules are not spherical or it may indicate dissociation. Calculation of the number of atoms in the molecules of the compounds examined was also made by means of Longinescu's expression (*Abstr.*, 1903, ii, 553; this vol., ii, 113), and in many cases indicates considerable dissociation. Freundler's observations are also in accord with this result (*Abstr.*, 1896, ii, 531).

L. M. J.

Solid Solutions and Isomorphism. GIUSEPPE BRUNI and MAURICE PADOA (*Gazzetta*, 1904, 34, i, 133—143).—In view of the fact that nitro-compounds are often isomorphous with the corresponding halogen compounds, the authors have made a series of

cryoscopic determinations with such derivatives, the following being the conclusions drawn from the results obtained. On dissolving a nitro-compound in the corresponding chloro-, bromo-, or iodo-derivative, a solid solution is generally obtained exhibiting very anomalous cryoscopic behaviour. If, however, the halogen compound is dissolved in the nitro-derivative, either slightly abnormal or normal cryoscopic behaviour is observed. The nitro-group must hence be placed in the isomorphogenous group containing the halogens and cyanogens.

T. H. P.

[Phase Rule.] RUDOLF WEGSCHEIDER (*Zeit. physikal. Chem.*, 1904, 47, 740—742).—A reply to Byk (this vol., ii, 313). J. C. P.

Chemical Equilibrium and Fall of Temperature. WALTHER NERNST (*Festschr. Ludwig Boltzmann*, 1904, 904—915).—The author reduces to mathematical formulæ the influence of a temperature gradient on the equilibrium of a chemical system. The phenomena of which the theory is here given are, for example, those observed in Deville's experiments with a hot-cold tube, but the experimental data by which the author's deductions are quantitatively tested are those referring to the thermal conductivity of nitrogen peroxide, a dissociating gas (see Magnanini and Malagnini, *Abstr.*, 1898, ii, 282; Magnanini and Zunino, *Abstr.*, 1900, ii, 525. Compare also Swart, *Abstr.*, 1891, 780). It is possible, with the author's formulæ, to calculate the thermal conductivity of nitrogen peroxide at various temperatures in good agreement with the experimental values.

J. C. P.

Equilibrium of a Solid with a Liquid Phase, chiefly in the Vicinity of the Critical State. JOHANNES D. VAN DER WAALS (*Arch. Neer.*, 1904, 9, ii, 158—185).—A paper largely mathematical and illustrated by numerous diagrams essential to its comprehension. An interesting point obtained is that in such equilibrium the phenomena of "retrograde solidification" should be frequently found, both by pressure change at constant temperature and by temperature change at constant pressure.

L. M. J.

Equilibria in the System $\text{NH}_4\text{NO}_3 + \text{AgNO}_3$. JAN VON ZAWIDZKI (*Zeit. physikal. Chem.*, 1904, 47, 721—728).—When silver nitrate is added to ammonium nitrate, the freezing point of the latter is lowered ultimately to a eutectic temperature 101.5° . This is followed by an intermediate branch of the freezing point curve which has its summit at 109.6° and 50 molecular per cent., thus corresponding with the formation and separation of the compound, $\text{NH}_4\text{NO}_3 \cdot \text{AgNO}_3$. A second eutectic point lies just beyond the summit, and thence the freezing point curve rises regularly to the freezing point of silver nitrate. The study of the freezing point phenomena has shown that no mixed crystals are formed, and this is confirmed by a determination of the transition points of ammonium nitrate and silver nitrate. The three transition points of ammonium nitrate lie at the same temperature levels (namely, 125.0° , 85.4° , and 35.0°) whatever the admixture of silver nitrate. A

similar remark applies to the transition point of silver nitrate at 159.6° . The determinations of these various transition points have been made thermometrically, and agree well with those made by earlier investigators. It is noted that the first branch of the freezing point curve shows a slight break at 125° , the highest transition point of ammonium nitrate.

J. C. P.

The Apparent Diminution of the Energy of a Weak Acid in the presence of one of its Normal Salts. GABRIEL CHESNAU (*Compt. rend.*, 1904, 138, 968—970).—The author has made a series of experiments on the influence of sodium acetate in promoting the precipitation of the sulphides of the metals of the iron group by hydrogen sulphide in the presence of acetic acid, and finds that it is the formation of an alkali sulphide by the action of hydrogen sulphide on sodium acetate even in the presence of free acetic acid which is the cause of the more or less complete precipitation of metallic sulphides in the presence of sodium acetate, which are not precipitated in the presence of acetic acid only, for a mixture of sodium acetate and hydrogen sulphide gives with sodium nitroprusside the purple colour characteristic of alkali sulphides, and the addition of increasing proportions of acetic acid retards, but does not suppress, this reaction.

M. A. W.

Velocity of Crystallisation of Isomorphous Mixtures. MAURICE PADOA (*Atti R. Accad. Lincei*, 1904, 13, i, 329—337).—The author has studied the alteration produced in the velocities of crystallisation of azobenzene, phenylpropionic acid, α -naphthylamine, dibenzyl, phenanthrene, tribromophenol, *m*-bromonitrobenzene, and bromocamphor by the addition of various compounds, including some which are isomorphous with those just named. The results show that the addition to a substance of substances which form solid solutions with it diminishes the velocity of crystallisation either not at all or only slightly. This may be employed as a convenient means of detecting isomorphism, as only small quantities of material are required. The addition of isomorphous substances to a compound does not exert any characteristic action on the formation of nuclei in the crystallisation.

T. H. P.

Catalytic Action of Platinum Black. RUDOLF VONDRÁČEK (*Zeit. anorg. Chem.*, 1904, 39, 24—40).—The various hypotheses respecting the catalytic action of platinum black, submitted by Bredig, Haber, and others, are mentioned. The author has examined the action of platinum black in promoting the decomposition of ammonium nitrate into nitrogen and water. A mixture of equivalent amounts of potassium nitrite and ammonium chloride in aqueous solution was used. The rate of decomposition is proportional to the quantity of platinum present when the solutions are not too concentrated, and it increases with increase of temperature.

There are two forms of platinum black, one of which contains oxygen and the other does not; the former can act as an oxidising and the latter as a reducing agent. It is shown that the former

variety can oxidise solutions of ammonia and ammonium salts with evolution of nitrogen, whilst the latter variety can reduce solutions of nitrous and nitric acids respectively, and, in so doing, is converted into the former variety. The same conversion can also be effected by atmospheric oxygen. When platinum black is left in contact with ammonium salts, it absorbs nitrogen, which is liberated by the action of aqueous potassium hydroxide solution. The decomposition of ammonium nitrite by platinum black proceeds in two stages: firstly, the platinum black, which, to begin with, contains oxygen, oxidises the ammonium nitrite, thus: $2\text{NH}_4\text{NO}_2 + x\text{PtO}_n + y\text{H}_2\text{O} = \text{N}_2 + 2\text{HNO}_2 + x\text{Pt} + (y+3)\text{H}_2\text{O}$, and, secondly, the nitrous acid formed in the first stage is reduced by the platinum, which is now oxygen-free, thus: $2\text{HNO}_2 + x\text{Pt} = \text{N}_2 + \text{H}_2\text{O} + x\text{PtO}_n$.

The catalytic action of platinum black on a mixture of hydrogen and oxygen is analogous; the platinum black is alternately reduced by hydrogen and oxidised by oxygen.

When ethyl alcohol was boiled with an aqueous solution of potassium chlorate in presence of platinum black, the chlorate was reduced, but there was no reduction in the absence of platinum. A similar reduction of chlorate took place when dextrose was oxidised by potassium chlorate in presence of platinum black. A. McK.

Inversion of Sucrose induced by the Platinum Metals. FRANZ PLZÁK and B. HUŠEK (*Zeit. physikal. Chem.*, 1904, 47, 733—739. Compare Šulc, Abstr., 1900, ii, 395).—Palladium powder, as usually obtained, markedly retards the inversion of sucrose by acids (compare Šulc, *loc. cit.*). This effect, however, is due to the presence of some foreign metal, probably zinc, and pure palladium actually accelerates the inversion of sucrose. The efficiency of palladium in inducing the sucrose inversion increases with the length of time for which it has been dried at 100° , an observation pointing to the oxide as the probable cause of inversion. When the palladium has been previously ignited in the air, its accelerating effect is slight until about three hours have elapsed. The catalytic efficiency of platinum is greater, that of iridium is less, than that of palladium under similar conditions. J. C. P.

Rapid Methods for the Physico-chemical Analysis of Physiological Liquids. PHILIPPE A. GUYE and STEFAN BOGDAN (*J. Chim. phys.*, 1903, i, 379—390).—The paper contains first an account of some modifications of customary apparatus to enable the constants of viscosity, conductivity, and cryoscopic depression to be determined speedily and with only a small quantity of liquid. The authors then describe the results of some experiments with normal and pathological urine, in which very great differences in the actual values of the physical constants and in the values per gram of dissolved matter are seen to exist. Variations in the physical constants are also found to ensue after the lapse of 12 hours, although no differences could be detected by analysis. They consider that the determination of such physical constants will be of great service in pathology, and further experiments are in progress. L. M. J.

Bibliography of Colloids. ARTHUR MÜLLER (*Zeit. anorg. Chem.*, 1904, 39, 121—151).—The literature in connection with colloids is embraced in the 356 publications which are enumerated.

A. McK.

Theory of Dyeing. I. Behaviour of Inorganic Colloids towards the Fibre. WILHELM BILTZ (*Ber.*, 1904, 37, 1766—1775).—It is demonstrated that inorganic colloids are more or less absorbed from solution by cotton yarn, wool, and especially silk, independently of the chemical nature of the dissolved colloids. The theory of dyeing is discussed at length, but for this the original should be consulted.

E. F. A.

Inorganic Chemistry.

The Atomic Weights of Oxygen and Hydrogen and the Probable Value of an Atomic Ratio. PHILIPPE A. GUYE and EDOUARD MALLET (*Compt. rend.*, 1904, 138, 1034—1037).—The arithmetic means of the values obtained by Morley for the atomic weight of oxygen ($H=1$) by three direct and independent methods are (1) 15·8791, from the ratio $O:H_2$; (2) 15·8785, from the ratio $H_2O:H_2$; (3) 15·8784, from the densities and volume ratio; and the difference between the two extreme values is 0·0007; if, however, Vallier's correction be applied to the arithmetic means, the numbers become 15·8789, 15·8786, and 15·8786 respectively, with a difference of 0·0003 between the extreme values, and the final value is $O=15·8787$ for $H=1$, or $H=1·00764$ for $O=16$. M. A. W.

Composition of Double Halogen Salts. HORACE L. WELLS (*Amer. Chem. J.*, 1904, 31, 395—398. Compare Abstr., 1902, ii, 11).—A criticism of Ephraim's generalisations (Abstr., 1903, ii, 418, 538, 552) relating to the formation of double halogen salts (compare also Grosmann, Abstr., 1903, ii, 476; and Pfeiffer, Abstr., 1903, ii, 596). E. G.

Solubility of Atmospheric Oxygen in Sea-water and in Water of Different Degrees of Salinity. FRANK CLOWES and J. W. H. BIGGS (*J. Soc. Chem. Ind.*, 1904, 23, 358—359).—Since determinations of the solubility of atmospheric oxygen in waters intermediate in salinity between distilled water and sea-water have not previously been made, results are recorded with samples of mixtures of distilled water and sea-water with the view of establishing standard percentages of aëration for estuary waters of varying salinity. Winkler's method was employed.

The amount of oxygen dissolved in sea-water gradually increases when the particular sample is repeatedly shaken with air at intervals

of some days. The maximum power of solution is accordingly attained only when the deoxidising agents, which are presumably present, are removed. The extent to which this deoxidation occurs is indicated by the tabulated results. The amount of chlorine in each sample is also quoted.

The solubility of atmospheric oxygen diminishes regularly in proportion to the amount of sea-water present. The sodium chloride in sea-water is the particular constituent which determines the amount of atmospheric oxygen dissolved.

A. McK.

Physical Constants at Low Temperatures. I. Densities of Solid Oxygen, Nitrogen, Hydrogen, &c. JAMES DEWAR (*Proc. Roy. Soc.*, 1904, 73, 251—261).—The densities have been calculated from the volume of gas which, when liquefied or solidified, just filled a cooled bulb of known capacity. The results obtained are summarised in the following table :

| Temp. | Densities. | | |
|----------|------------|-----------|-----------|
| | Oxygen. | Nitrogen. | Hydrogen. |
| – 182.5° | 1.1181 | — | — |
| – 195.5 | 1.1700 | 0.8042 | — |
| – 210.5 | 1.2386 | 0.8792 | — |
| – 252.5 | 1.4256 | 1.0265 | 0.0700 |
| – 258.3 | — | — | 0.0754 |
| – 259.9 | — | — | 0.0763 |

With the help of these densities, the author has constructed Mathias' rectilinear diameters for oxygen, nitrogen, and hydrogen respectively, and shows that the values thence deduced for the critical densities of these gases agree well with those arrived at by other observers. With these rectilinear diameters, it is also possible to calculate the molecular volumes at absolute zero, the vapour density being neglected, and the author accordingly finds 21.21, 25.49, and 24.18 as the molecular volumes at – 273° of oxygen, nitrogen, and hydrogen respectively.

J. C. P.

Calorimetric Measurements with Liquid Oxygen and Liquid Nitrogen. HEINRICH ALT (*Ann. Physik*, 1904, [iv], 13, 1010—1027) — The latent heat of vaporisation r has been determined at a number of temperatures for liquid oxygen and liquid nitrogen by supplying electrically a known amount of heat to the liquid and finding the corresponding loss of weight of the latter. Allowance is, of course, made for the normal loss due to conduction of heat from the surroundings. In the case of oxygen, the value of r at the boiling point (– 182.4°) is 52.02 ± 0.15 cal.; under reduced pressures and at correspondingly lower temperatures, r increases, especially at the lowest temperatures, until at – 201.3° it has a value about 59.0 cal. The latent heat of vaporisation of nitrogen has at its own boiling point (– 195.67°) the value 48.58 ± 0.18 cal., increases in a linear manner as the temperature of vaporisation is lowered, and at – 210° has the value 52.06 cal.

With the same apparatus, by supplying electrically the heat necessary to raise the liquid from the boiling point under a low pressure to the boiling point under atmospheric pressure, the author has determined the mean specific heats of liquid oxygen and liquid nitrogen. The values found are: for oxygen, 0.347 ± 0.014 (temperature range -200° to -183°); for nitrogen, 0.430 ± 0.008 (temperature range -208° to -196°), the same value as that obtained by Dewar.

J. C. P.

Production of Active Oxygen and the Hypothesis of Electrons. WILLEM P. JORISSEN (*Chem. Centr.*, 1904, i, 1055—1056; from *Chem. Weekblad.*, 1, 337—342. Compare Abstr., 1897, ii, 253).—Experiments made with an apparatus similar to that used by Helmholtz and Richarz have shown that triethylphosphine, benzaldehyde, oil of turpentine, and a strong solution of sodium sulphite tend to condense water vapour; radium bromide and a 30 per cent. solution of hydrogen peroxide also have a similar effect. A photographic plate in a light tight case was found to be affected by phosphorus which was undergoing spontaneous oxidation.

E. W. W.

Melting Point Lines of the System, Sulphur + Chlorine. H. W. BAKHUIS ROOZEBOOM and A. H. W. ATEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 6, 599—605. Compare Abstr., 1903, ii, 634).—The equilibrium between S_2Cl_2 , SCl_2 , SCl_4 , and Cl_2 is not changed when the liquid mixture is cooled below 0° to temperatures at which a solid phase separates. Mixtures containing 50—100 per cent. of sulphur behave like mixtures of the type $S_2Cl_2 + S$. The solubility of sulphur in sulphur chloride is very slight at low temperatures. The results are represented graphically. The true melting point of sulphur tetrachloride is not known; the crystals of sulphur tetrachloride, when rapidly heated, are quite permanent up to -20° .

A. McK.

Influence of Hydriodic Acid on the Oxidation of Sulphurous Acid. ARMAND BERG (*Compt. rend.*, 1904, 138, 907—909. Compare Abstr., 1903, ii, 179).—Comparable experiments made on the rate of oxidation of sulphurous acid in the presence of air, with and without the addition of hydriodic acid, show that for each strength of sulphurous acid there is a certain limiting proportion of hydriodic acid which has no influence on the oxidation of the former, but that the hydriodic acid has a retarding or accelerating effect according as it is present in proportions less or greater than this limit. For a 4 per cent. solution of sulphurous acid, this limiting value of the hydriodic acid solution is 3 per cent., which corresponds with about $1HI$ to $3H_2SO_3$, whilst for the same strength of sulphurous acid the amounts of oxygen absorbed (1) by the sulphurous acid alone, (2) in the presence of 0.36 per cent. of hydriodic acid, (3) in the presence of 36.5 per cent. of hydriodic acid, are as 8 : 1 : 89.5.

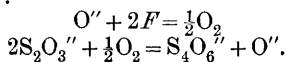
Manganous chloride, ferrous chloride, or solutions of the metallic iodides behave similarly to hydriodic acid in accelerating the oxidation

of sulphurous acid, whilst potassium chloride or bromide has no action, and hydrochloric acid retards the oxidation, and even stops it altogether.

M. A. W.

Electrolytic Oxidation of Sodium Thiosulphate and the Mechanism of the Process. C. J. THATCHER (*Zeit. physikal. Chem.*, 1904, 47, 641—720).—When sodium thiosulphate is oxidised electrolytically at a platinised electrode, tetrathionate alone is produced if the solution remains neutral or very faintly alkaline. If the solution is, or becomes, acid or strongly alkaline, other reactions take place, resulting in the formation of sulphur, sulphite, and sulphate. That sulphate is formed in a strongly alkaline solution is probably due to the presence of trithionate, which, along with thiosulphate, is produced by the hydrolysis of tetrathionate under these conditions; the trithionate so formed is then oxidised to sulphate. Sodium tetrathionate itself cannot be further oxidised either in neutral or acid solutions.

The electrolytic oxidation of thiosulphate to tetrathionate, which takes place with an anode potential difference of from -0.75 to -0.95 volt, is regarded not as resulting from direct electrolytic action ($2\text{S}_2\text{O}_3'' + 2F = \text{S}_4\text{O}_6''$), but as being a secondary chemical process brought about by some oxidising agent (probably oxygen) which is itself primarily formed in the electrolysis. This chemical oxidation is accelerated by the platinised electrode, for if the platinum is clean and bright, the amount of oxidation for the same amount of electricity is much smaller. That the oxidation of thiosulphate is an indirect process is deduced firstly from a study of the variation of the potential-current curves with the concentration of the various ions involved (compare Cottrell, *Abstr.*, 1903, ii, 258); by this means, it is shown that hydroxyl or oxygen ions are discharged at the electrode. Further, the influence of certain non-dissociated "poisons," such as mercuric cyanide, on the potential difference between platinum and thiosulphate solutions shows that in the process $\text{S}_2\text{O}_3'' \rightarrow \text{S}_4\text{O}_6''$ oxygen or some compound of oxygen is involved, and that the metal of the electrode acts catalytically. In view of these results, the mechanism of the electrolytic oxidation of thiosulphate may be represented as follows:



J. C. P.

Density of Nitrogen at the Temperature of Liquid Air, and its Relation to the Pressure. A. BESTELMEYER and SIEGFRIED VALENTINER (*Sitzungsber. K. Akad. München*, 1903, 743—755).—Density determinations have been carried out at temperatures between 81° and 85° absolute, and under pressures varying from 160 to 1320 mm. of mercury. With the help of a coefficient of expansion, the observations have been reduced to the two temperatures 81.4° and 85° absolute. At each temperature, the product pv diminishes as p increases, the relation between these two quantities being a linear one.

J. C. P.

Influence of Pressure on the Ratio c_p/c_v for Nitrogen at the Temperature of Liquid Air. SIEGFRIED VALENTINER (*Sitzungsber. K. Akad. München*, 1903, 691—741).—At the temperature of liquid air, the ratio of the specific heats of nitrogen increases with the pressure to the extent of 5 per cent. over a range of 2 atmospheres. It is very probable that the value of the ratio at the temperature of liquid air and low pressures is the same as the value at the ordinary temperature and atmospheric pressure. J. C. P.

Solubility of Nitrogen in Liquid Oxygen. ALFRED STOCK (*Ber.*, 1904, 37, 1432—1434).—A criticism of Erdmann and Bedford's paper (this vol., ii, 328). G. Y.

Constitution of Nitrogen Sulphide. OTTO RUFF and EMIL GEISEL (*Ber.*, 1904, 37, 1573—1595).—Nitrogen sulphide has been shown by Schenck (*Abstr.*, 1896, i, 426) to have the molecular formula N_4S_4 , and was represented by him by the structural formula $S < \begin{smallmatrix} N \\ \text{---} \end{smallmatrix} S < \begin{smallmatrix} N \\ \text{---} \end{smallmatrix} S$. The researches of Ruff on sulphur haloids (*Abstr.*, 1903, ii, 204, 590) render the bivalence of sulphur in this and similar compounds improbable.

Nitrogen sulphide is best prepared by Schenck's method, and the relation of the yield to the composition of the sulphur chloride employed indicates that it is the sulphur tetrachloride present which is concerned in the reaction: $12SCl_4 + 16NH_3 = 3S_4N_4 + 48HCl + 2N_2$.

Dry hydrogen chloride reacts with nitrogen sulphide according to the equation $N_4S_4 + 12HCl = 4NH_3 + 4S + 12Cl$, no free nitrogen being produced.

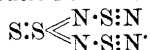
Nitrogen sulphide dissolves in liquid anhydrous ammonia at -40° to a red solution, and on evaporation of the ammonia an orange or brown powder remains, containing up to 2 mols. of NH_3 , but dissociating slowly, even at the ordinary temperature. Solutions of metallic iodides in anhydrous ammonia form precipitates with the nitrogen sulphide. Lead iodide forms *lead dithiodi-imide*, $PbN_2S_2NH_3$, crystallising in olive-green prisms, becoming orange in air without alteration of weight, decomposing when slowly heated, and exploding very violently at 140° when rapidly heated. Hydrogen chloride reacts quantitatively according to the equation $PbN_2S_2NH_3 + 6HCl = PbCl_2 + 3NH_3 + 2S + 4Cl$. Dry liquid hydrogen sulphide reacts thus: $PbN_2S_2NH_3 + 3H_2S = PbS + 4S + 3NH_3$. Ethyl iodide forms ethyl sulphide and lead iodide.

Mercury thiodi-imide, $HgN_2S_2NH_3$, prepared in similar manner from mercuric iodide, forms bright yellow crystals and resembles the lead compound, but contains one atom of sulphur less. The addition of lead iodide to the filtrate from the mercury compound produces a precipitate of lead dithiodi-imide, and, conversely, mercuric iodide precipitates mercury thiodi-imide from the filtrate from the lead compound. Definite compounds could not be obtained from other metallic iodides.

Water hydrolyses nitrogen sulphide, forming sulphuric, sulphurous, thiosulphuric, and trithionic acids. Alkalis form only sulphurous and

thiosulphuric acids with small quantities of hydrogen sulphide and perhaps of dithionic acid.

The most probable constitution for nitrogen sulphide is



The compound with ammonia may be assumed to dissociate in anhydrous ammonia solution into $\text{N:S}\cdot\text{NH}_2$ and $\text{S:S}(\text{NH})_2$, of which the former yields an insoluble mercuric salt, $\text{N:S}\cdot\text{NHg}$, and the latter an insoluble lead salt, $\text{S:S} \begin{array}{c} \text{N} \\ \text{N} \end{array} \text{Pb}$.

C. H. D.

Graphitic Acid or Oxide. FREDERIC S. HYDE (*J. Soc. Chem. Ind.*, 1904, 23, 300—302).—The various methods of preparing graphitic acid are discussed. The author modifies Fitzgerald's method by carrying out the oxidation of graphite with a mixture of concentrated sulphuric and nitric acids and potassium chlorate at 60° instead of by heating over the water-bath, as Fitzgerald does. Ceylon graphite produces the best results; the grass-green oxide initially formed is more readily produced than with artificial graphite, whilst with ordinary coke, charcoal, or carbon black it is not formed at all.

A. McK.

Carbides and Silicides. A General Method for the Determination of Carbon in Carbides. WALTHER HEMPEL [and PAUL RUCKTÄSCHEL] (*Zeit. angew. Chem.*, 1904, 17, 296—301, 321—325).—The author now publishes an account of Rucktäschel's experiments (*Inaug. Diss. Rostock*, 1892), since they are of interest as being an extension of Moissan's researches.

Details of the preparation and properties of various carbides are given. Carbides of iron, containing 1·84, 2·37, 3·02, 2·34, 3·13, 4·01, and 4·96 per cent. of carbon respectively, were prepared in the electric furnace. With cobalt, alloys were prepared containing 0·44, 0·62, 1·87, 1·88, 2·65, 2·80, 6·47, and 8·45 per cent. of carbon respectively, and with nickel, alloys containing 1·71, 2·14, 4·69, and 6·25 per cent. of carbon respectively. In the nickel alloys, the carbon is in the state of mechanical admixture, whilst in the iron and cobalt alloys a large proportion of the carbon is chemically combined with the metal. An alloy of platinum, containing 1·2 per cent. of carbon, was prepared. Copper formed an alloy containing 0·03 per cent. of carbon; manganese, silver, gold, chromium, and tungsten formed alloys containing 0·47, 0·04, 0·31, 2·23, and 3·3 per cent. of carbon respectively.

Alloys of silicon and cobalt, containing 2·70, 11·6, and 19·3 per cent. of silicon respectively, were prepared by fusing a mixture of reduced cobalt and of powdered silicon which had been crystallised from zinc. Alloys of silicon and nickel, containing 3·5, 13, and 19·95 per cent., alloys of silicon, carbon, and cobalt, and alloys of silicon, carbon, and nickel, were prepared.

The amount of carbon was estimated by Weyl's method. In the case of those metals which were insoluble in the commoner mineral acids, the alloy was heated in a sealed tube with almost the theoretical amount of aqua regia.

A. McK.

Action of Silicon on Water at a Temperature of about 100°. HENRI MOISSAN and F. SIEMENS (*Compt. rend.*, 1904, 138, 939—941).—When pure amorphous or crystalline silicon in a fine state of division is kept in a glass vessel in contact with distilled water at a temperature of about 95° for 6 to 12 hours, each particle of silicon becomes coated with hydroxide, which can be detected by Vigouroux's method (compare Abstr., 1895, ii, 447) and confirmed by analysis, and at the same time bubbles of gas are given off which consist of hydrogen and a little air. This apparent decomposition of water by silicon is, however, due to traces of alkali furnished by the glass, which reacts with the silicon to form a soluble silicate with the liberation of hydrogen, for if the glass vessel is replaced by one of platinum and the water is distilled from a platinum retort, or if the glass vessel is used and a trace of hydrofluoric acid added to the water, the silicon remains unchanged and no gas is evolved; whilst the addition of a drop of alkali to the distilled water in the platinum vessel causes the decomposition to proceed as in the first case. Using a fused quartz vessel and water distilled from a platinum retort the silicon is not attacked.

These experiments show the importance of the warning issued by the International Commission on Atomic Weights against the use of glass vessels for exact analytical work. M. A. W.

Synthesis of Silicon Hydride, SiH_4 , from the Elements. A. DUFOUR (*Compt. rend.*, 1904, 138, 1040—1042).—When pure hydrogen prepared by electrolysis, freed from oxygen by passing it through a silica tube heated to redness, and from moisture by cooling it in liquid air, is passed over silicon heated to above its fusing point by means of an electric arc or an oxyhydrogen blowpipe flame, the two combine to a slight extent, and silicon hydride can be detected in the escaping gases by the formation of a black precipitate with silver nitrate, of a reddish-brown precipitate with copper sulphate, and of silica capillaries when the gas is allowed to bubble through water. The product was identified with the hydride SiH_4 by cooling the mixed gases in liquid air under a pressure of 20 atmospheres in a special apparatus; by this means a small drop of limpid liquid was obtained, the boiling point of which, as determined by a thermoelectric couple, was found to be -114° under 750 mm. pressure. The boiling point of silicon hydride, SiH_4 , prepared from magnesium silicide by the action of hydrochloric acid (compare Moissan and Smiles, Abstr., 1902, ii, 318), is -115° to -116° under 730 mm. pressure. M. A. W.

Reduction of Silica by Hydrogen. A. DUFOUR (*Compt. rend.*, 1904, 138, 1101—1103).—When a current of hydrogen is passed through a silica tube heated to softness by an oxyhydrogen blowpipe flame, a deposit of silicon and silica or of silica only is formed on the inside of the tube, due to the reduction of the silica by the hydrogen at the high temperature with the formation of silicon hydride and water vapour, and at a slightly lower temperature the reverse reaction in which silica and hydrogen are formed. When the reverse reaction is incomplete, part of the silicon hydride is decomposed yielding silicon and hydrogen, which accounts for the mixed deposit of silicon and

silica. If a rod of silica be heated to softness in an oxyhydrogen blowpipe flame, it loses in weight, a rod weighing 970 mg. losing 500 mg. in 15 minutes.

Against the view that these phenomena can be explained by the volatility of the silica and its partial dissociation under the conditions of the experiment, the author advances the following facts: (1) silica is not appreciably volatile at the temperature of the experiment (compare Moissan, *Abstr.*, 1893, ii, 532. Compare, however, Moissan, *Abstr.*, this vol., ii, 256); (2) when, in the first experiment, the hydrogen is replaced by oxygen or carbon monoxide, no deposit is formed in the tube; (3) in the second experiment, the loss in weight of the silica rod varies with the nature of the gas employed as a source of heat, being greatest for a mixture of oxygen and hydrogen, less for a mixture of oxygen and coal gas, and least for a mixture of oxygen and carbonic oxide; (4) if a current of nitrogen is passed through a heated quartz tube, no deposit is formed, showing that there is no tendency for the silica to dissociate at that temperature. M. A. W.

Experiments on the Light Phenomena caused by Ozone and by Radium. FRANZ RICHARZ and RUDOLF SCHENK (*Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 13, 490—493. Compare this vol., ii, 154).—The illuminating effect caused by the action of ozone on zinc blende is contrasted with that caused by radium in an atmosphere of air or of oxygen. Ozone formation occurs even with feebly radioactive specimens of radium bromide in an atmosphere of oxygen. Since ozone causes zinc blende to luminesce, it follows that part of the luminescence undergone by zinc blende under the influence of radium in the presence of air must be due to ozone. An experiment is described to show that the fluorescence of zinc blende in the presence of radium in an atmosphere of dry carbon dioxide is not so marked as when dry air is substituted for carbon dioxide. Barium platino-cyanide, which does not luminesce in ozone, luminesces under the influence of radium to the same extent in air and in carbon dioxide. The luminescence of zinc blende caused by ozone is regarded as an oxidation phenomenon.

Other substances, for instance, red phosphorus and turpentine, are also found to behave like zinc blende towards ozone. A. McK.

Electrolytic Enriching of Radium from Radium-Barium Preparations. EDGAR WEDEKIND (*Chem. Zeit.*, 1904, 28, 269—270).—Radium-barium chloride, freshly prepared from crude radium-barium carbonate, was electrolysed, the cathode being mercury and the anode platinum. The amalgam, formed at the beginning of the electrolysis, was more strongly radioactive than that subsequently formed.

A. McK.

Radioactivity in relation to the Presence of Helium. RAFFAELLO NASINI (*Atti R. Accad. Lincei*, 1904, [v], 13, i, 217—218).—The mud and waters of Abano (compare Nasini and Anderlini, *Abstr.*, 1894, ii, 422; with Salvadori, *Abstr.*, 1898, ii, 527), when acidified with hydrochloric acid, give with barium chloride a precipitate

which is strongly radioactive; a much less active substance, however, is obtained on precipitating the same solution with sulphuric acid. The mud of Abano is much more radioactive than that of Battaglia; detritus obtained from the *soffioni* of Larderello is also active. Barium sulphate obtained from a Vesuvian rock containing both helium and barium possesses a high activity. W. A. D.

Action of Sodium Amalgam on Solutions of Potassium Salts and of Potassium Amalgams on Solutions of Sodium Salts. G. McPHAIL SMITH (*J. Physical Chem.*, 1904, 8, 208—213).—The retarding effect of solutions of potassium and sodium salts on the action of sodium and potassium amalgams on water was considered by Fernekcs (this vol., ii, 163) to be opposed to the ionic theory—for although the effect of sodium salts on the action of sodium amalgam is explicable, that of potassium salts is not. The author shows that the facts are not opposed to the ionic theory, inasmuch as the first action may be regarded as between the potassium ions of the solution and the sodium atoms of the amalgam until equilibrium is reached, in accordance with the mass action law, when the sodium-potassium amalgam reacts with the water. Experiments show that when a sodium amalgam is placed in a solution of a potassium salt a mixed amalgam is soon formed, and the same holds for a potassium amalgam placed in a solution of a sodium salt. This principle is, further, the basis of the preparation of various amalgams. L. M. J.

Solubility of Acid Nitrates. ERICH GROSCHUFF (*Ber.*, 1904, 37, 1486—1493).—Ammonium trinitrate, $\text{NO}_3\text{NH}_4 \cdot 2\text{NO}_3\text{H}$, crystallises in prismatic needles melting at $29-30^\circ$; the labile dinitrate, $\text{NO}_3\text{NH}_4 \cdot \text{NO}_3\text{H}$, forms irregular hexagonal platelets. The solubility of these compounds in nitric acid at various temperatures has been determined. Potassium trinitrate crystallises in prisms melting at 22° ; potassium dinitrate, $\text{NO}_3\text{K} \cdot \text{NO}_3\text{H}$, crystallises in plates, forms a eutectic mixture with the trinitrate melting at 22° , and at 29° decomposes into the normal salt and an acid solution. Curves are plotted showing the behaviour of these salts towards nitric acid and water, and the results are discussed from the standpoint of the equilibrium theory. E. F. A.

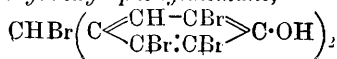
Action of Silica on the Melting of Alkali Carbonates. NICOLAUS M. VON WITTORF (*Zeit. anorg. Chem.*, 1904, 39, 187—196).—Mallard showed that the quantity of carbon dioxide evolved by the action of silicon dioxide on an excess of molten sodium carbonate increases with rise of temperature and finally reaches a limit in cases where the amount of carbon dioxide is less than that corresponding to the formation of an orthosilicate, $2\text{Na}_2\text{O} \cdot \text{SiO}_2$, in the molten mass (this Journ., 1873, 135, 243). The author has examined the equilibrium between carbon dioxide and silica when these competed for the same alkali oxide. A mixture of sodium carbonate and silica was heated in a covered platinum crucible until constant in weight, the partial pressure of the carbon dioxide amounting to 0.07 atmosphere. As soon as equilibrium was established, a stream of dry carbon dioxide was introduced into the crucible, which was

Behaviour of Phenol Ethers on Distillation with Zinc Dust. HERMANN THOMS (*Arch. Pharm.*, 1904, 242, 95—98).—Contrary to the opinion usually held, anisole (methoxybenzene) is decomposed in part when it is mixed with zinc dust and distilled. In all, 60 grams of anisole were distilled in portions of 2·5 grams; ethylene was formed, and 20 grams of liquid distillate were obtained, from which about 3 grams each of benzene and phenol, 2·5 grams of diphenyl, and 10 c.c. of unchanged anisole were isolated. C. F. B.

Preparation of Ethers by means of Magnesium Compounds and Halogen Methyl Ethers, XCH_2OR . JULES HAMONET (*Compt. rend.*, 1904, 138, 813—814).—By a modification of Henry's method for preparing ethers from halogen methyl ethers (compare Heury, *Abstr.*, 1892, 27), namely, the substitution of Grignard's organo-magnesium compounds for the organo-zinc compounds, the author has obtained a better yield of the ether, 60—65 per cent. of the theoretical in the case of the open chain compounds, but much less in the case of the ring compounds. The reaction, which is represented by the equation $RMgX + XCH_2OR = MgX_2 + CH_2ROR$, proceeds more readily with the bromo-derivative of the methyl ether than with the chloro- or iodo-compound, and the bromomethyl ethers are prepared by the action of hydrobromic acid on the corresponding chloro-compounds. The action of bromomethyl ether, CH_2BrOMe , and bromomethyl amyl ether, $CH_2BrO \cdot C_5H_{11}$ (a liquid boiling at 74—76° under 18 mm. pressure), on the magnesium derivatives of ethyl bromide, phenyl bromide, and benzyl chloride was studied, and the following ethers were prepared: propyl amyl ether, $C_3H_7O \cdot C_5H_{11}$, boiling at 130°, benzyl methyl ether, CH_2PhOMe , boiling at 170°, and *phenylethyl methyl ether*, $OMe \cdot CH_2 \cdot CH_2Ph$, a colourless liquid boiling at 189—190°. M. A. W.

Action of Bromine and Chlorine on Phenols: Substitution Products, ψ -Bromides, and ψ -Chlorides. X. Action of Bromine on *p*-Dihydroxydiphenylmethane. THEODOR ZINCKE and R. KRÜGENER (*Annalen*, 1903, 330, 61—81).—Tetrabromo-*p*-dihydroxydiphenylmethane is readily prepared by treating dihydroxydiphenylmethane in acetic acid solution with bromine (compare Staedel, *Abstr.*, 1878, 420); it melts at 226—227°, and yields an *acetyl* derivative when acted on with acetic anhydride in the presence of sulphuric acid, which crystallises in needles melting at 167—168°. When the tetrabromide is left in contact with bromine for 24 hours, a *hexabromide*, $CH_2(C \begin{smallmatrix} \text{CH}=\text{CBr} \\ \text{CBr} \cdot \text{CBr} \end{smallmatrix} > C \cdot OH)_2$, is formed, which crystallises in colourless needles melting at 204°, and is not acted on by reducing agents or by sodium methoxide; its *diacetyl* derivative crystallises in needles melting at 215°.

*ψ -Heptabromo-*p*-dihydroxydiphenylmethane,*



complex ion. The value for $[D]$ can be determined in such solutions, where the whole of the metal is in solution, as a complex salt. The determination of $[R]$, the non-metallic portion of the complex ion, is more difficult. For the discussion of this and other difficulties, such as the uncertainty of the degree of electrolytic dissociation of the complex salt, reference should be made to the original paper.

During the measurements, it is necessary to take precautions that no atmospheric oxygen is in solution, since the silver electrodes, in the presence of oxygen, are readily soluble in the electrolytes used, more particularly in solutions of potassium cyanide; hence the values obtained cannot be constant if air is present in the solutions. The apparatus used is depicted. Solutions of silver iodide in potassium iodide were first examined where, in one limb of the apparatus, the concentration of the potassium iodide was the same, but that of the silver iodide was different from those in the other limb. The following relationship was accordingly obtained: $[M_1]/[M_2] = \sqrt[n]{[D_1][D_2]}$. The ratio $[M_1]:[M_2]$ of the free silver ions was deduced from Nernst's formula for the value of the concentration cell. The values quoted show that in the more dilute solutions examined the complex ion contains 2 atoms of silver and that, in the solutions richer in potassium iodide, other complex ions are present which contain only one atom of silver. A second class of concentration cells was next examined, where the concentration for the complex salt was equal, but that for potassium iodide varied; in this case, there was evidence for the existence in solution of compounds of the types $K_2Ag_2I_4$, $K_3Ag_2I_5$, $K_4Ag_2I_6$, and $K_5Ag_2I_7$, whilst K_3AgI_4 is possibly present in the more concentrated solutions. The concentration of silver ions in $N/1$ potassium iodide solution is 8.9×10^{-17} , a value in agreement with that deduced from solubility determinations. From measurements of silver potassium thiocyanates, it is deduced that the complex ion contains only one atom of silver and that the formulæ of the complex salts are $K_3Ag(CNS)_4$ and $KAg(CNS)_2$. It is not probable that ions of the type $Ag(CNS)_3$ occur. Salts of the type $K_3Ag(CNS)_4$, when dissolved, decompose into the salts $KAg(CNS)_2$ and $KCNS$. Silver chloride dissolves in potassium thiocyanate solution with difficulty. Measurements, next made with silver potassium cyanides, showed that the compounds $KAg(CN)_2$ and $K_2Ag(CN)_3$ were present in solution. Silver cyanide of the type $AgCN$ cannot exist in aqueous suspension; the solid, stable silver cyanide has the formula $Ag_2Ag(CN)_2$. The formation of nitrile from potassium cyanide and isonitrile from silver cyanide may be accounted for by the author's observations. The relationships which obtain by interaction of an $N/0.1$ solution of potassium cyanide with equivalent amounts of silver chloride, bromide, and iodide respectively are also considered. The action of sulphuric acid on silver silver cyanide is thus represented: $H_2SO_4 + Ag_2Ag(CN)_2 = Ag_2SO_4 + 2HCN$. Potassium silver cyanide is the best electrolyte for the silver voltameter, provided that no oxygen is present. The $E.M.F.$ of silver towards a potassium cyanide solution which is less than $N/0.05$ is represented by $E = 0.444 - 0.056 \log [Ag(CN)_2'] : [CN']^2$; this value is smaller than that obtained for zinc, copper, or gold in potassium cyanide solutions.

Silver chloride and silver bromide have a very slight tendency to form complex ions. A. McK.

Action of Iodine on Silver Nitrite. WILHELM NEELMEIER (*Ber.*, 1904, 37, 1386—1388).—A carbon tetrachloride solution of iodine, when shaken during some 3 days with solid silver nitrite, gives a theoretical yield of nitric peroxide according to the equation $I_2 + 2AgNO_2 = 2AgI + N_2O_4$. The peroxide was estimated by taking an aliquot part of the brown solution, shaking with excess of dilute sodium hydroxide solution, estimating the total nitrogen as ammonia, and the nitrite by permanganate. It was not found possible to obtain dinitryl, $NO_2 \cdot NO_2$, a compound isomeric with the peroxide. J. J. S.

The Existence of Mono-ammoniacal Silver Nitrate. ALBERT REYCHLER (*J. Chim. phys.*, 1903, i, 345—357).—Crystallisation of a concentrated solution of molecular quantities of silver nitrate and ammonia yields a product which seems to be $AgNO_3 \cdot NH_3$. Kuriloff has shown that the product varies in composition, and regards it as a mixture of silver nitrate with the di-ammonia-compound, $AgNO_3 \cdot 2NH_3$. The author confirms these results and finds that the composition varies with the quantities of the constituents employed, and that with small excess of ammonia the crystals contain considerably more of this compound than is represented by $AgNO_3 \cdot NH_3$. The quantity of silver oxide precipitated by ammonia is in fair agreement with the equation $AgNO_3 + AgNO_3(NH_3)_2 + H_2O \rightleftharpoons Ag_2O + 2NH_4 \cdot NO_3$. The mixture of the constituents in the crystals is, however, so intimate that the author views the substance as a solid solution. L. M. J.

A New Method of forming Calcium Carbide. L. M. BULLIER (*Compt. rend.*, 1904, 138, 904—905).—The author points out that the method of preparing calcium carbide by electrolysis of the chloride in a graphite crucible described by Moissan (compare this vol., ii, 333) is not new, and only differs in a few unimportant details from the method which he patented in 1895. M. A. W.

Decomposition of Barium Nitrate by Heat. B. N. GOTTLIEB (*Chem. Zeit.*, 1904, 28, 356).—Barium nitrate was heated in a platinum boat at various temperatures, the gas evolved in each particular experiment being measured and analysed. For the purpose of regenerating nitric acid from barium nitrate, it is best to heat the latter very quickly to a high temperature. A. McK.

Action of Dry Hydrogen Chloride dissolved in Anhydrous Benzene on Dry Zinc. KAUFMAN G. FALK and CAMPBELL E. WATERS (*Amer. Chem. J.*, 1904, 31, 398—410. Compare Patten, *Abstr.*, 1903, ii, 417).—An account is given of a number of experiments carried out with the object of determining the action of dry hydrogen chloride dissolved in anhydrous benzene on zinc. In the earlier experiments, it was found that, although great care was taken to avoid the introduction of moisture, a slight action always occurred, bubbles of

hydrogen being evolved and a protective coating of chloride being formed on the zinc. This action usually continued for 2—3 hours.

The later experiments showed that the more completely the dehydration was effected, the less was the action which took place. In those cases in which the greatest precautions were adopted, the white coating was not produced, but the surface of the zinc became darkened and the formation of hydrogen bubbles ceased within an hour.

E. G.

Zinc-aluminium Alloys. HECTOR PÉCHEUX (*Compt. rend.*, 1904, 138, 1103—1104).—Zinc and aluminium form nine well-defined alloys corresponding with the formulæ Zn_3Al , Zn_2Al , ZnAl , ZnAl_2 , ZnAl_3 , ZnAl_4 , ZnAl_6 , ZnAl_{10} , and ZnAl_{12} , with the sp. gr. at 16° of 5.704, 5.488, 4.639, 3.685, 3.638, 3.400, 3.140, 3.084, and 3.040 respectively; the melting points lie between those of zinc and aluminium, and increase from Zn_3Al to ZnAl_{12} . All the alloys are brittle, the first two are the hardest, the last three the softest; the first two also present a crystalline surface on fracture, the rest do not; the first three are slightly sonorous, the remaining six possess a good resonance. All the alloys are readily attacked by concentrated or dilute hydrochloric acid, by concentrated sulphuric acid, by hot nitric acid, concentrated or dilute, or by hot concentrated potassium hydroxide solution. Concentrated nitric acid attacks only the first three, and concentrated potassium hydroxide solution attacks only Zn_2Al , ZnAl , ZnAl_2 , ZnAl_3 , and ZnAl_4 in the cold. The alloys are not attacked by hydrogen sulphide in the cold, or by distilled water in the cold or at 100° .

M. A. W.

Lead-aluminium Alloys. HECTOR PÉCHEUX (*Compt. rend.*, 1904, 138, 1042—1044).—The ingot obtained by cooling a fused mixture of lead, sp. gr. 11.23, and aluminium, containing 2 per cent. of iron and traces of carbon and silicon, sp. gr. 2.67, is made up of three layers, the lower and upper consisting of pure lead and aluminium respectively, the middle one being an alloy of the two metals containing 90 to 97 per cent. of aluminium, according to the rate of cooling and the hygrometric state of the mould. The specific gravities of the alloys decrease with the increase in the proportion of aluminium, the alloys containing 93, 95, and 98 per cent. of aluminium, having sp. grs. of 2.745, 2.674, 2.600 respectively, whilst the melting points increase. The colour of the alloys resembles that of aluminium, but is less bright; they are malleable, pliable, less hard than aluminium, can be engraved, and present a close granular structure on breaking. Each alloy is merely a molecular juxtaposition of the two metals, for on melting and drawing into rods of much smaller diameter the composition is altered, the alloy becoming richer in lead; thus, from the three alloys containing respectively 93, 95, and 98 per cent. of aluminium, three new ones were obtained containing 92, 94, and 96 per cent. of aluminium and having sp. grs. of 2.765, 2.691, and 2.671 respectively. In respect of their chemical properties, the alloys are not acted on by moist air; hydrochloric acid dissolves the

aluminium at 13°; concentrated sulphuric acid dissolves both metals, liberating hydrogen at 13° and sulphur dioxide on heating; concentrated nitric acid has very little action at the ordinary temperature, but an energetic one on heating; the dilute acid has little or no action; concentrated potassium hydroxide or aqua regia dissolves them readily in the cold; hydrogen sulphide blackens the alloys containing 92 to 93 per cent. of aluminium, and distilled water is without action even at 100°.

M. A. W.

Dissociation of Lead Nitrate. LEO BAEKELAND (*J. Amer. Chem. Soc.*, 1904, 26, 391—399).—When pure lead nitrate, enclosed in a vacuum, sealed glass tube, is heated at 357°, decomposition takes place and the tube becomes filled with red fumes. On allowing the tube to cool slowly, the red vapour gradually disappears and the vacuum is re-established. These changes are due to the reversible reaction, $\text{Pb}(\text{NO}_3)_2 \rightleftharpoons \text{PbO} + \text{O} + 2\text{NO}_2$.

This reaction has been investigated with a view to determine the dissociation pressure at different temperatures and the influence of an excess of either of the gaseous products on it. The special apparatus devised for these experiments is described in detail with the aid of diagrams. It was found that at temperatures between 223° and 448° the pressure of the evolved gases gradually increased to a maximum and then remained constant. This limiting pressure, which represents the pressure of dissociation of lead nitrate, varies with the temperature and is practically constant for each temperature. The value of this dissociation pressure at different temperatures is as follows. At 223°, 6.2 mm.; at 230°, 6.9 mm.; at 250°, 11.8 mm.; at 274°, 32.6 mm.; at 296°, 78.4 mm.; at 357°, 514.0 mm.; and at 448°, 1180.0 mm.

If the gaseous products of the dissociation are removed and the residue is again heated until the maximum pressure is attained, it is found that the dissociation pressure remains constant until the lead nitrate has suffered considerable decomposition. At a certain point, the partially decomposed salt shows a large decrease in its dissociation pressure, which at 357° suddenly falls from 514 mm. to 260 mm. The residue is now of a slightly yellow colour and has the composition of a basic lead nitrate, $3\text{PbO}, 2\text{N}_2\text{O}_5$.

If the apparatus is left in communication with the vacuum pump for 10 days, during which period the lead nitrate is maintained at a temperature of 357°, the residue afterwards undergoes no further decomposition at this temperature, shows no dissociation pressure, and has the composition $3\text{PbO}, \text{N}_2\text{O}_5$. This basic salt is decomposed at a red heat with formation of lead oxide.

Experiments were undertaken with the object of determining the influence of the relative proportions of nitrogen peroxide and oxygen in the gaseous products on the dissociation pressure of lead nitrate. The results are tabulated, and show that the introduction of variable amounts of oxygen and nitrogen peroxide before applying heat to the tube containing the salt occasions a considerable decrease in the dissociation pressure.

E. G.

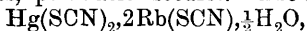
Interaction of Sodium Arsenate and Lead Acetate. LEONARD DOBBIN (*Pharm. J.*, 1904, [iv], 18, 582—583).—The quantitative test prescribed by the B.P. for ascertaining the purity of sodium arsenate has been investigated and found to be substantially, but not strictly, accurate. When sodium arsenate and lead acetate react in aqueous solution, the precipitate consists chiefly of normal lead arsenate, although the liquid becomes slightly acid owing to the liberation of acetic acid. If, however, the precipitation is effected in presence of added acetic acid, lead hydrogen arsenate, PbHAsO_4 , is the main product of the reaction. E. G.

Copper and Oxygen. E. HEYN (*Zeit. anorg. Chem.*, 1904, 39, 1—23).—The freezing point curves of mixtures of copper and cuprous oxide, where the maximum amount of cuprous oxide used in any experiment was 9 per cent., have been determined with the view of deciding whether the liquid solution solidifies to a broken or to an unbroken series of mixed crystals. It was found that the series of mixed crystals was a broken one; the curve deduced from the experimental results is discussed from the standpoint of Roozeboom's criteria. In the transition from the liquid to the solid state, the solubility of copper in cuprous oxide is practically nil. After solidification, copper and cuprous oxide both separate, that is, there are two solid phases. Pure copper solidifies at 1103° . The eutectic point, where 3.4—3.5 per cent. of oxide is present in the alloy, is 1084° . All other alloys melt within a range of a few degrees, the lower limit being 1084° . The observed depressions of melting point are in accordance with the calculated values.

The solid phases which separated during solidification were also examined microcrystallographically. A. McK.

Double Salts of Rubidium and Bivalent Mercury. HERMANN GROSSMANN (*Ber.*, 1904, 37, 1258—1260).—On adding mercuric iodide to a hot concentrated solution of rubidium iodide until saturation is reached and then cooling, the compound $\text{HgI}_2 \cdot \text{RbI}$ separates in bright yellow, prismatic needles. The compound $\text{HgI}_2 \cdot 2\text{RbI}$ is obtained from a solution containing molecular quantities of the components, and forms large, yellow, four-sided plates. A salt corresponding with the caesium compound, $\text{HgI}_2 \cdot 3\text{CsI}$, could not be obtained.

Rubidium mercury trithiocyanate, $\text{Hg}(\text{SCN})_2 \cdot \text{Rb}(\text{SCN})$, prepared by dissolving mercuric thiocyanate in aqueous rubidium thiocyanate, forms long, colourless, prismatic needles. The salt,



formed on mixing the components in molecular proportions, separates in large, colourless, monoclinic plates.

Rubidium thiocyanate mercuric cyanide, $\text{Hg}(\text{CN})_2 \cdot \text{Rb}(\text{SCN})$, can be recrystallised from hot water, and forms long, colourless needles. The analogous *pyridine* compound, $\text{Hg}(\text{CN})_2 \cdot (\text{C}_5\text{H}_6\text{N})\text{SCN}$, prepared from its components, closely resembles it. W. A. D.

Metals of the Cerium Group. WILHELM MUTHMANN and L. WEISS (*Annalen*, 1904, 331, 1—46. Compare Abstr., 1902, ii, 262; 1903, ii, 212).—The oxides of the cerium group of metals have been

separated by a modification of the Demarcay-Drossbach method: each operation, 5 kilos. of the oxides are dissolved in excess of warm nitric acid, and magnesium carbonate added to the solution until it is alkaline to congo-red. On dilution and boiling, the iron, aluminium, manganese, silica, and phosphoric acid are precipitated together with some of the alkaline earths. The mother liquor is evaporated, when crystals of the double nitrates, $2\text{M}(\text{NO}_3)_3 \cdot 3\text{Mg}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$, separate. These crystals, together with further crops obtained from the mother liquor, are then fractionally crystallised. After 15 crystallisations, the least soluble fraction is colourless, and the most readily soluble, in which samarium can be detected by the spectroscope, orange-red.

After prolonged fractionation of the intermediate fractions, the following five fractions were obtained: (i) lanthanum with small quantities of cerium and praseodymium, (ii) praseodymium, together with small quantities of cerium, lanthanum, and neodymium, (iii) praseodymium and neodymium, (iv) neodymium with small quantities of praseodymium and samarium, (v) samarium and neodymium with gadolinium, yttrium, erbium, and holmium.

The first fraction was freed from cerium by electrolytic oxidation to ceric salts and separation as ceric magnesium nitrate from a solution in concentrated nitric acid. Any cerium remaining in solution was precipitated by permanganate and sodium carbonate. The mother liquor yielded pure lanthanum, in the least soluble salt. From the second fraction, the cerium and then the lanthanum were separated, and finally the praseodymium fractionated from the neodymium; the praseodymium thus obtained contained only a trace of lanthanum. Fraction (iv), which was very large in quantity, was used as a source of neodymium, the praseodymium being separated first. Finally, a neodymium oxide was prepared which contained 99.5 per cent. of the oxide, and was quite free from praseodymium when examined spectroscopically. Fraction (v) was carefully fractionated, and finally small quantities of samarium oxide isolated from it. In the course of the fractionation, examination of the ultraviolet spectrum served to show when the neodymium had been eliminated. The erbium was separated from the samarium by taking advantage of the fact that the double nitrate of the former is more readily soluble; the samarium was separated from the yttrium earths by fractionation of the oxalates. Evidence was obtained that the erbium consists of at least two elements.

The metals were prepared by electrolysis of the anhydrous chlorides in an enlarged and improved apparatus (compare *loc. cit.*). By this means, large quantities of pure cerium were prepared from the chloride without the addition of alkali or barium chlorides. Since the metals lanthanum, neodymium, and praseodymium melt at a higher temperature than cerium, whilst their chlorides melt at a lower temperature, a higher temperature was required in the neighbourhood of the electrodes in order that a regulus of metal might be formed; this was secured by using very slender carbon electrodes or by using an iron rod to which sticks of carbon were fastened. Lanthanum was isolated by using a current of 50 amperes and 10–15 volts, and neodymium a current of 90–100 amperes and 16–22 volts. In the

case of praseodymium, it was necessary to avoid the formation of the dioxide, and consequently a maximum current of 70 amperes was used.

The metals were purified by remelting in crucibles made of pure magnesia, and covered by a layer of barium chloride; ordinary crucibles cannot be employed, as lanthanum, neodymium, and praseodymium attack silicates.

Metallic samarium can only be prepared with difficulty by electrolysis of the fused chloride, which is a pale yellow, hard powder, mixed with one-third of its weight of barium chloride, using a current of 100 amperes and a small carbon cathode. The metal is deposited on the carbon, from which it is separated by a golden-yellow carbide. Samarium is a pale grey, lustrous metal, which rapidly becomes yellow from oxidation in the air, has the hardness of steel, and is extremely brittle; its sp. gr. is 7.7—7.8.

A comparison of the physical properties of cerium, lanthanum, neodymium, and praseodymium shows that polished surfaces of the metals are very similar, but exhibit minute differences: lanthanum has the whiteness of tin, cerium that of iron; neodymium has a yellow tinge, which is still more strongly marked in the case of praseodymium. With the exception of lanthanum, these metals are permanent in the air. The following shows the increasing order of hardness: Pb, Sn, Ce, La, Zn, Nd, Pr, Sm. The sp. gr. of cerium is 7.0424; lanthanum, 6.1545; neodymium, 6.9563; praseodymium, 6.4754. It is shown that on plotting the atomic volumes against the atomic weights, cerium, and not lanthanum, occupies an exceptional position. The melting points, which were observed by heating the metals under a layer of potassium and sodium chloride in a crucible of magnesia with a weighted rod of magnesium resting on the surface of the metal, are, for cerium, 623°; lanthanum, 810°; neodymium, 840°; and for praseodymium, 940°. The temperature was measured by a platinum-platinum-rhodium junction to an accuracy of about 10°.

The heats of combustion, owing to the readiness with which these elements can be burnt in air, can be measured in a Berthelot-Mahler calorimeter. The heats of combustion referred to 1 gram of the metal are, for cerium (burning to CeO_2), 1603.15 cal.; for lanthanum, 1602.1; for neodymium, 1506; and for praseodymium, 1476.8 cal.; the three metals last mentioned give the sesquioxide. The high values of the heat of combustion suggest that these metals would be useful reducing agents, since a mixture of the cerium and yttrium groups of metals can be easily obtained. The heat of combustion of such a mixture is, for 1 gram, 1655.5 cal.

K. J. P. O.

Alloys of Cerium and Lanthanum. WILHELM MUTHMANN and H. BECK (*Annalen*, 1904, 331, 46—57. Compare preceding abstract).—When cerium is introduced into aluminium molten in a crucible under a mixture of potassium and sodium chloride, a very great development of heat is observed, the metals being heated to redness. At the same time, a small amount of hydrogen is given off, possibly from the

cerium. The product is a mixture of aluminium and a compound, CeAl_4 , which remains in needles or prisms when the metal is treated with an alkali hydroxide. The alloy is brittle, crystallises in the rhombic or monoclinic system [$a:b=0.7706:1$], and has a sp. gr. 4.193. The heat of combustion for 1 gram is 3441.19 cal., whereas the calculated value is 3940.5, hence the heat of formation is +499.3 cal., a fact which accounts for the high temperature which results on mixing the molten metals.

Lanthanum forms with aluminium an alloy, LaAl_4 , which is isomorphous [$a:b=0.7517:1$] with the cerium alloy; its sp. gr. is 3.923, and the heat of combustion 3481.6 cal., and the heat of formation +395.4 cal. These alloys are extremely stable, are not affected by exposure to the air, are not attacked by nitric acid, but are dissolved by hydrochloric acid and potassium hydroxide although far less readily than their components.

The alloys of cerium and magnesium are regarded as solid solutions, and are formed with an absorption of heat, 84.9 cal. being absorbed in the formation of 1 gram of the alloy of the composition Ce 46.94 and Mg 52.76 per cent. The alloy is silver-white and extremely brittle, and has a sp. gr. 2.744; it does not change in the air, but burns with an intensely bright flame. It is readily dissolved by dilute acids, hydrogen being evolved; its heat of combustion is 3952.4 cal. per gram.

Zinc and cerium combine explosively, forming an alloy containing Ce 32.75 and Zn 66.26 per cent. It is bluish-white, of high melting point, and very brittle. It oxidises readily when exposed to the air, and dissolves easily in dilute acids. The heat of combustion is 1305.5 cal., and the heat of formation +94.48 cal. for 1 gram.

All these alloys combine with hydrogen at 200–400°, forming the hydrides of cerium and lanthanum. At 900°, the alloy of cerium and magnesium interacts with nitrogen, the nitrides of the two metals being produced.

A liquid amalgam of cerium, containing 2.74 per cent. of the metal, and a solid amalgam, containing 10.41 per cent., can be prepared by adding cerium to boiling mercury in an atmosphere of carbon dioxide. They react with water with the evolution of hydrogen, and become covered with a very voluminous coat of ceric hydroxide in moist air; spontaneous combustion frequently takes place.

K. J. P. O.

Hydrides and Nitrides of Neodymium and Praseodymium.
WILHELM MUTHMANN and H. BECK (*Annalen*, 1904, 331, 58–59. Compare preceding abstracts).—*Neodymium hydride*, NdH_2 (?), is formed when strips of neodymium are heated in hydrogen at 220°, and is a brittle indigo-blue solid, which, when heated in air, is converted into a mixture of nitride and oxide. *Praseodymium hydride*, PrH_3 (?), is an amorphous, green solid. *Neodymium nitride*, NdN , formed by direct combination at 900°, is black, easily pulverised, and reacts with water with the evolution of ammonia. The *praseodymium nitride*, PrN , is quite similar.

K. J. P. O.

[Preparation of Metals, Metalloids, Alloys.] WILHELM MUTHMANN (*Annalen*, 1904, 331, 60—63. Compare preceding abstracts).—Escales' patent (D.R.-P. 1903, 145820) for the use of alloys of the cerium group of metals with each other or with aluminium or magnesium as reducing agents is criticised. Attention is drawn to the fact that it is not at present possible, as Escales suggests, to partially remove cerium by electrolysis of the mixed oxides, and then to reduce lanthanum and didymium oxides in the same manner. Such a decomposition has not yet been achieved. The *E.M.F.* necessary for the reduction of the chlorides (CeCl_3 , 2.46 volts; LaCl_3 , 2.40 volts; NdCl_3 , 2.25; and PrCl_3 , 2.26 volts) emphasise this fact.

K. J. P. O.

Indium. ALFRED THIEL (*Zeit. anorg. Chem.*, 1904, 39, 119—120. Compare this vol., ii, 177).—The value previously quoted by the author for the atomic weight of indium is too small. Later determinations made with indium tribromide give the value 114.81 ± 0.07 .

Indium salts suffer considerable hydrolytic dissociation.

According to potential measurements of indium in solutions of the chloride, the solution tension of the metal amounts to 10^2 — 10^3 atmospheres: indium is accordingly intermediate between iron and lead. Indium can be quantitatively determined electrolytically with a silvered platinum cathode.

A. McK.

Soluble Ferric Potassium Arsenite. LEONARD DOBBIN (*Pharm. J.*, 1904, [iv], 18, 585).—When freshly precipitated ferric arsenite, prepared by the interaction of potassium arsenite and ferric chloride, is added to a solution of potassium hydroxide until no more will dissolve, and the resulting solution is evaporated gently to dryness on glass or porcelain plates, a lustrous, amorphous, reddish-brown substance, $6\text{K}_2\text{O}, 5\text{Fe}_2\text{O}_3, 9\text{As}_2\text{O}_3, 24\text{H}_2\text{O}$, is obtained, which dissolves readily in water, forming a strongly alkaline solution. Ferric arsenite is also soluble in concentrated ammonia and yields a product which resembles the potassium compound in appearance, but is insoluble in water.

E. G.

Ammonium Salt of Chromatodiperacid. KARL A. HOFMANN and H. HIENDLMAIER (*Ber.*, 1904, 37, 1663—1667).—An ammonium salt, $\text{CrO}_2(\text{O} \cdot \text{O} \cdot \text{NH}_4)_2$, of chromatodiperacid is obtained when chromic hydroxide, mixed into a paste with water, is oxidised at 0° with hydrogen peroxide and then mixed with 10 per cent. ammonium hydroxide also at 0° . It forms dark red, octahedral crystals, and on exposure to the air, or on solution in water at the ordinary temperature, evolves oxygen (about 18 per cent.), yielding ammonium chromate. It is highly explosive when heated, hammered, or moistened with a drop of concentrated sulphuric acid, but is only slowly decomposed in cold 10 per cent. ammonium or potassium hydroxide. It may also be prepared by oxidising an aqueous solution of ammonium dichromate with hydrogen peroxide in presence of ammonia.

The addition of dilute sulphuric acid to the ammonium salt produces the blue colour characteristic of perchromic acid, but this is fugitive

and quickly changes to green. The addition of dilute acetic acid gives a blue colour due to ammonium perchromate, which is not extracted by ether.

A constitutional formula $\text{CrO}_3 \cdot \text{O} \cdot \text{ONH}_4$, containing a heptavalent chromium atom, is suggested for Wiede's (Abstr., 1898, ii, 28, 295; 1899, i, 244) blue perchromates. J. J. S.

Complex Inorganic Acids. IX. FRIEDRICH KEHRMANN and BERNHARD FLÜRSCHHEIM (*Zeit. anorg. Chem.*, 1904, **39**, 98—107).—The salt to which Marignac assigns the formula $4\text{K}_2\text{O}, \text{SiO}_2, 12\text{WO}_3 + \text{aq.}$ has, according to the authors, the formula $7\text{K}_2\text{O}, 2\text{SiO}_2, 20\text{WO}_3$. It is formed in accordance with the equation $2(2\text{K}_2\text{O}, \text{SiO}_2, 12\text{WO}_3) + 7\text{K}_2\text{CO}_3 = 7\text{K}_2\text{O}, 2\text{SiO}_2, 20\text{WO}_3 + 4\text{K}_2\text{WO}_4 + 7\text{CO}_2$. The separation of tungstic and silicic acids may be effected by the action of aqueous hydrofluoric acid on the mixed oxides. The separation of the complex acid from alkalis is conducted by precipitation with quinoline hydrochloride. The authors confirm the observations of Marignac with regard to the compounds $2\text{K}_2\text{O}, \text{SiO}_2, 12\text{WO}_3 + \text{aq.}$ and $2\text{K}_2\text{O}, 2\text{H}_2\text{O}, \text{SiO}_2, 12\text{WO}_3 + \text{aq.}$

By the action of potassium carbonate on the former of these compounds, crystals of the compound $7\text{K}_2\text{O}, 2\text{SiO}_2, 20\text{WO}_3 + \text{aq.}$ are obtained, from which the duodeci-salt may be regenerated by the action of hydrochloric acid.

From the analytical figures obtained, it is supposed that silicic acid, in the moment of its liberation from its salts by strong acids, is volatile. A. McK.

Complex Salts of Quadrivalent Tin. ARTHUR ROSENHEIM and HANS ARON (*Zeit. anorg. Chem.*, 1904, **39**, 170—174).—Whilst in aqueous solution chlorostannic acid suffers partial hydrolytic dissociation, the latter is more marked with bromostannic acid, whilst iodo-stannic acid is practically completely hydrolytically dissociated.

When an alcoholic solution of pyridine hydriodide is added to the dark brown solution obtained by dissolving tin tetraiodide in an alcoholic solution of hydrogen iodide, the *pyridine stanni-iodide*, $\text{C}_5\text{H}_7\text{N}_2, \text{H}_2\text{SnI}_6$, separates in bluish-black, glistening needles, which, after a time, decompose with separation of iodine. The *quinoline* salt, obtained in an analogous manner, forms black needles, from which iodine also gradually separates.

The optical activity of *d*-tartaric acid is increased by the addition of stannic chloride. Addition of gradually increasing amounts of an aqueous solution of potassium hydroxide and stannic chloride brought about a distinct rise in the specific rotation; in one set of experiments, the $[\alpha]_D$ at 18° increased from 14.27° to 27.44° , whilst in another set it increased from 12.80° to 45.98° ($t = 15^\circ$). It is concluded that one atom of quadrivalent tin unites with one molecule of tartaric acid to form a complex ion (compare Henderson, Orr, and Whitehead, *Trans.*, 1899, **75**, 554).

Potassium stannitartrate, $\text{K}_2(\text{SnO})\text{C}_4\text{H}_2\text{O}_6, 5\text{H}_2\text{O}$, is prepared by evaporating an aqueous solution of *d*-tartaric acid (1 mol.), stannic chloride (1 mol.), and potassium hydroxide (6 mols.) to small bulk, and

then adding alcohol. *Sodium stannitartrate* was prepared in an analogous manner. A. McK.

[Titanous Sodium Sulphate.] PETER SPENCE & SONS, LD. (D.R.-P. 149602).—*Titanous sodium sulphate*, $\text{Ti}_2\text{Na}_2(\text{SO}_4)_4 \cdot 5\text{H}_2\text{O}$, is obtained by electrolysing a solution containing titanic sulphate, sodium sulphate, and sulphuric acid. The crystalline basic sodium titanic sulphate may be used for the preparation of the solution. The electrolysis is carried out in a lead-lined vessel with diaphragm, a low current-density being employed. On evaporating until the sp. gr. is 1.145, the new salt crystallises. It is a powerful reducing agent, and may also be applied in the preparation of other titanous compounds. It differs from the titanium alums in the quantity of water of crystallisation, and also in its crystalline form. C. H. D.

Electromotive Behaviour of Vanadium. LUIGI MARINO (*Zeit. anorg. Chem.*, 1904, 39, 152—169).—Since certain vanadium compounds resemble the corresponding compounds of phosphorus and arsenic, and certain others, on the other hand, are analogous to the corresponding chromium compounds, the author has studied the electromotive character of vanadium itself as contrasted with that of chromium, phosphorus, and arsenic respectively.

The specimen of vanadium employed contained 8.66 per cent. of carbon and 1.6 per cent. of other impurities. It was insoluble in hydrogen haloids, but soluble in hot sulphuric acid (2 vols. acid : 1 vol. water), and when the temperature was further raised to 330°, vanadic acid was formed, whilst the odour of sulphur dioxide was perceptible. Nitric acid of sp. gr. 1.18 readily acts on it to form vanadium nitrate of the type VX_4 , whilst vanadic acid is formed from the action of nitric acid of sp. gr. >1.35. Vanadic acid is also formed when chloric, perchloric, and bromic acids respectively are employed. Vanadium is attacked by a warm solution of ammonium persulphate, whilst the liquid becomes strongly acid owing to the formation of Caro's acid and sulphuric acid. Vanadic acid is also produced by the action of saturated solutions of potassium chlorate, bromate, iodate, and perchlorate respectively, for instance, $5\text{KClO}_3 + 6\text{V} = 5\text{KCl} + 3\text{V}_2\text{O}_5$. Vanadium remains unchanged in solutions of the alkali chlorides, bromides, iodides, sulphates, acetates, and oxalates and in solutions of various other salts. Solutions of mercuric chloride, cupric chloride, and ferric chloride are reduced by vanadium to mercurous chloride, cuprous chloride, and ferrous chloride respectively. Vanadium reduces solutions of gold chloride, silver nitrate, platinic chloride, and iridium tetrachloride. Vanadium dioxide ferrocyanide is produced when a solution of a chloride, nitrate, or sulphate is added to a solution of potassium ferricyanide containing vanadium.

When an electrolyte, which has no action on vanadium at the ordinary temperature, is electrolysed with a vanadium anode, a complex vanadium anion is produced, the vanadium going into solution as a quadri-valent ion. The loss of weight of the anode is always greater than that corresponding with the amount of silver separated in the voltmeter ; this is due to the oxidation of carbon to carbon dioxide. In

alkaline solutions, vanadium dissolves as $Va^{1/5}$, independently of concentration, temperature, and current density. Potential measurements were made according to the scheme, $V | MX | NaNO_3 | AgNO_3 | Ag$, where $X = Cl, Br, OH$, and $M = Na, K, Zn, Mg, \&c.$; with the exception of the cases of sodium and potassium hydroxides, the *E.M.F.* was independent of the nature of the electrolyte. The *E.M.F.* of the combination $V | MX | H_2CrO_4 | Pt$ was also determined. In no case did the vanadium become passive.

In electromotive character, vanadium is not analogous to chromium, but to arsenic and phosphorus.

A. McK.

Catalytic Decomposition of Antimony Hydride. MAX BODENSTEIN (*Ber.*, 1904, 37, 1361—1368).—The decomposition of antimony hydride, which is accelerated by the action of the antimony produced, is a case of "autocatalysis." The experimental results obtained by Stock and Guttman (this vol., ii, 246) are shown by means of a number of tables to accord well with theory. The catalytic action of the antimony is found to be proportional to its mass rather than to its surface, but this is consistent with surface action if the antimony is deposited in the form of numerous small particles. Whether what is measured is the velocity of reaction or of diffusion is difficult to decide; a determination of the temperature-coefficient, which is large in the case of the decomposition of arsenic and phosphorus hydrides, would be valuable.

C. H. D.

Interaction between Bismuth Oxyhaloids and an Aqueous Solution of Potassium Hydroxide. WALTER HERZ and G. MUHS (*Zeit. anorg. Chem.*, 1904, 39, 115—118).—Bismuth oxychloride was shaken with potassium hydroxide in a thermostat at 30° , when the presence of chlorine ions was soon detected in the solution. It was found that the equilibrium, $BiOCl + KOH \rightleftharpoons BiO \cdot OH + KCl$, was attained. Since, according to the law of mass action, $[KOH] = k[KCl]$, it was only necessary to estimate the concentration of alkali before and after shaking. The results obtained, however, with a large concentration of alkali are to be accounted for only on the assumption of some secondary reaction.

Bismuth oxychloride assumes a greyish-yellow colour on treatment with alkali.

The behaviour with bismuth oxybromide and potassium hydroxide was analogous.

A. McK.

Colloidal Gold. MAURICE HANRIOT (*Compt. rend.*, 1904, 138, 1044—1046. Compare Abstr., 1903, ii, 368, 543, 597).—Colloidal gold, prepared by Henrich's method (compare Abstr., 1903, ii, 299), is a bluish-violet powder, slightly soluble in pure water, readily so in alkalis, especially ammonia, insoluble in acids or their normal alkali salts. Acids precipitate it from alkali solution in a hydrated form which, when dried at 100° , is no longer soluble in alkalis, but when dried at 40° temporarily loses its solubility in alkalis, but recovers it on long contact with water. The substance dried at 40° contains 2.04 per cent. of water which it loses at 100° , 6.31 per cent. which it

loses at a red heat, 91.53 per cent. of gold, and 0.39 per cent. of sulphur trioxide; it has acid properties, forming salts with certain heavy metals, thus, when a solution of a copper salt is added to an ammoniacal solution of colloidal gold, a precipitate soluble in ammonia, but insoluble in water or potassium hydroxide, is obtained; when dried at 40°, the precipitate becomes insoluble in ammonia, and hydrochloric acid removes copper from it, leaving colloidal gold. Silver nitrate gives a brown coloration with a solution of colloidal gold; the further addition of ammonium nitrate gives a red precipitate soluble in pure water, and containing about 2 per cent. of silver. Lead acetate gives a precipitate with colloidal gold, which is insoluble in ammonia, whilst mercuric chloride gives no precipitate. Colloidal gold does not dissolve in mercury, and when strongly heated in a vacuum 1 gram of the substance gives off 5.2 c.c. of carbon dioxide, 5.4 c.c. of carbonic oxide, and 7.6 c.c. of hydrogen.

M. A. W.

Liquid Hydrosol of Gold. ALEXANDER GUTBIER and F. RESENSCHECK (*Zeit. anorg. Chem.*, 1904, 39, 112—114. Compare Abstr., 1902, ii, 610).—When gold chloride solutions are reduced by phenylhydrazine hydrochloride, the liquid hydrosol of gold so prepared was found to assume various colours, red, reddish-violet, violet, bluish-violet, blue, and even green, in various preparations. The dependence of the colour of the hydrosol on the concentrations of the solutions of gold chloride and phenylhydrazine hydrochloride has now been examined. The dialysed solutions are remarkably stable; they can be filtered and boiled, when the hydrogel can be obtained. The colloidal solutions are decolorised when they are shaken with animal charcoal or barium sulphate. From a solution of gold chloride, it is possible to obtain first the red, then the violet, and finally the blue hydrosol of gold; a lecture experiment is described to illustrate this.

A. McK.

Electrolytic Solution of Platinum. New Method of Preparing Platinocyanides. ANDRÉ BROCHET and JOSEPH PETIT (*Compt. rend.*, 1904, 138, 1095—1097. Compare this vol., ii, 229, 230).—Platinum behaves like iron or cobalt in respect to its solubility in potassium cyanide under the influence of an alternating current; with platinum electrodes of 5 sq. cm. area, in a 4 *N*-potassium cyanide solution, and with a current density of 20 to 80 amperes per square decimetre and a frequency of 42, 10 to 15 per cent. of the theoretical quantity of platinum passes into solution, whilst only 1 per cent. is dissolved in concentrated hydrochloric acid under similar conditions. If, instead of potassium cyanide, the equivalent of barium cyanide is employed, with a current density of 15 to 60 amperes per square decimetre, 7.5 to 11 per cent. of the theoretical quantity of platinum is dissolved, according to the equation $\text{Pt} + 2\text{Ba}(\text{CN})_2 + 2\text{H}_2\text{O} = \text{BaPt}(\text{CN})_4 + \text{Ba}(\text{OH})_2 + \text{H}_2$, and this forms a convenient method of preparing barium platinocyanide. The solubility of platinum and iron varies but little with the density of the current, whilst the solubility of cobalt increases with an increase in the current density.

M. A. W.

Preparation of Potassium Platinosochloride. PETER KLASON (*Ber.*, 1904, 37, 1360—1361).—According to a private communication from Heraeus, potassium platinosochloride is technically prepared by passing sulphur dioxide into a solution of chloroplatinic acid, heated on the water-bath until a sample gives no precipitate with ammonium chloride. A hot solution of twice the calculated quantity of potassium chloride is then added, and the potassium platinosochloride which separates is washed with alcohol and dried in the absence of light. Potassium platinichloride is less suitable than the acid as a starting-point.

Vezev has found (*Abstr.*, 1899, i, 572) that potassium oxalate reduces potassium platinichloride quantitatively. This reaction, however, does not occur in pure platinum solutions, but is dependent on the presence of iridium as a catalytic agent. A solution of potassium platinichloride and oxalate is not altered by boiling, but evolution of carbon dioxide commences immediately on the addition of a solution containing iridium. In presence of much iridium, the reaction may even become violent.

C. H. D.

Mineralogical Chemistry.

Mineral Analyses. FRANK W. CLARKE (*Bull. U. S. Geol. Survey*, 1903, 220, 1—119).—A collection is given of 507 analyses of minerals, most of them previously published, which have been made in the laboratory of the United States Geological Survey during the years 1880—1903. Over 150 distinct species are represented. L. J. S.

Presence of Argon in the Gases of the Fumeroles of Guadeloupe. HENRI MOISSAN (*Compt. rend.*, 1904, 138, 936—938).—Two specimens of gas were analysed: the first, from the *Fumerolle du Nord*, collected in a depression of the earth full of water at 96°, was saturated with water vapour, contained traces of hydrogen chloride and sulphur vapour, but no hydrocarbons, hydrogen, or carbon monoxide; the percentage composition of the gas was as follows: hydrogen sulphide, 2·7; carbon dioxide, 52·8; oxygen, 7·5; nitrogen, 36·07; argon, 0·73 (compare this vol., ii, 29); the small quantity of water accompanying the gas had an acid reaction, contained hydrogen sulphide, a trace of hydrogen chloride, and traces of iron, chalk, and sulphur in suspension. The second specimen came from the *Fumerolle Napoléon*, was also saturated with water vapour, contained traces of sulphur vapour, but no hydrogen chloride, hydrogen, hydrocarbons, or carbon monoxide, the percentage composition of the gas being hydrogen sulphide, 4·5; carbon dioxide, 69·5; oxygen, 2·7; nitrogen, 22·32; argon, 0·68; the acid liquid remaining in the flask in which the gas had been collected contained no hydrogen chloride, but a considerable quantity of sulphuric acid, and held in suspension sulphur, small quantities of calcium salts, and sesquioxide of iron.

The result of the analyses points to these gases belonging to those volcanic gases in which the carbon compounds are completely burned owing to access of air.

M. A. W.

Specific Gravity of Sylvite, Bischofite, and Carnallite. Origin of Bischofite. CARL PRZIBYLLA (*Centr. Min.*, 1904, 234—241).—Determinations of specific gravity, by weighing pure crystallised material in petroleum, gave: sylvite (KCl), 1·9872; bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), 1·5907; carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), 1·6018. The sum of the molecular volumes of sylvite and bischofite is 165·39, whilst the molecular volume of carnallite is 173·57; the application of pressure on carnallite would therefore result in the formation of sylvite and bischofite. Although bischofite is the last salt to separate from a saline solution, it is not always met with at the top of the salt deposits, and its occurrence in veins (not beds) of crushed carnallite and other salts is explained as a result of pressure.

From the difference in the amounts of heat absorbed when a mixture of sylvite and bischofite and when carnallite are dissolved in water, the heat of formation of carnallite from sylvite and bischofite is calculated as approximately 23·6 Cal.

L. J. S.

Realgar from Allchar, Macedonia. VICTOR GOLDSCHMIDT (*Zeit. Kryst. Min.*, 1904, 39, 113—121).—A crystallographic study. An analysis, by P. Jannasch, of the material examined crystallographically gave results in close agreement with the formula AsS . An analysis of realgar from the Binnenthal, Switzerland, is also given.

L. J. S.

Analysis of Lorandite from Allchar, Macedonia. PAUL JANNASCH (*Zeit. Kryst. Min.*, 1904, 39, 122—124).—Analysis of material which had been crystallographically examined by V. Goldschmidt gave the following results, agreeing with the formula TiAsS_2 previously assigned to this mineral (*Abstr.*, 1896, ii, 30):

| Tl. | As. | S. | Gangue. | Total. |
|-------|-------|-------|---------|--------|
| 58·75 | 21·65 | 19·26 | 0·08 | 99·74 |
| 59·08 | 21·32 | 18·75 | 0·12 | 99·27 |

L. J. S.

Zinc Ores of North Arkansas. JOHN C. BRANNER (*Trans. Amer. Inst. Mining Engin.*, 1902, 31, (1901), 572—603).—Eight analyses of sphalerite from different mines in this region show 64·48—66·2 per cent. of zinc, with only small amounts of impurities, ferric oxide for example, amounting to 0·15—0·62 per cent. Analyses of smithsonite gave the results under I—III, the last being of a yellow variet known as "turkey-fat."

| | ZnO. | CO ₂ . | H ₂ O. | SiO ₂ . | MgO. | CaO. | Fe ₂ O ₃ , Al ₂ O ₃ . | CdO. | Total. |
|------|-------|-------------------|-------------------|--------------------|------|------|---|-------|--------|
| I. | 64·31 | 34·93 | 0·58 | 0·10 | 0·03 | 0·90 | 0·12 | trace | 100·97 |
| II. | 62·20 | 33·86 | 2·30 | 0·02 | 0·18 | 1·25 | 0·21 | trace | 100·02 |
| III. | 63·84 | 34·60 | 1·09 | 0·25 | 0·07 | 0·70 | 0·42 | 0·90 | 101·87 |

L. J. S.

Manganiferous Carbonates from Kuttenberg, Bohemia. A. BUKOVSKÝ (*Jahrb. Min.*, 1903, ii, Ref. 338; from *Programm. d. Oberrealschule in Kuttenberg*, for 1902, 12 pp.; *Anz. III Congr. böhm. Naturf. u. Aertze, Prag*, 1901, 293).—The following analyses are given of the portions soluble in hydrochloric acid of: I, II, small, rhombohedral crystals of brown-spar; formula, $2\text{CaFe}(\text{CO}_3)_2, 3\text{CaMg}(\text{CO}_3)_2$. III, cleavage masses of ankerite, $5\text{Ca}(\text{Fe}, \text{Mn})(\text{CO}_3)_2, 4\text{CaMg}(\text{CO}_3)_2$. IV, rose-red manganocalcite, $7\text{CaCO}_3, \text{MnCO}_3$. V, ferruginous manganodolomite ("kutnohorite"), in large, cleavage masses of a white colour with a rosy tinge; $\text{Ca} : \text{Mn} : \text{Fe} : \text{Mg} = 7 : 5 : 1 : 2$. VI, similar to the last, but finer grained; $\text{Ca} : \text{Mn} : \text{Fe} : \text{Mg} = 3 : 1 : 1 : 1$. Analyses are also given of altered manganiferous carbonates.

| | CaCO_3 . | MgCO_3 . | FeCO_3 . | MnCO_3 . | Total. | Sp. gr. |
|------|-------------------|-------------------|-------------------|-------------------|--------|---------|
| I. | 55.69 | 20.52 | 21.98 | 1.13 | 99.32 | 2.95 |
| II. | 52.16 | 24.07 | 21.79 | 1.35 | 99.37 | — |
| III. | 51.49 | 17.28 | 25.80 | 4.84 | 99.41 | 3.05 |
| IV. | 85.02 | 0.45 | 0.86 | 13.77 | 100.10 | 2.775 |
| V. | 44.02 | 11.04 | 6.88 | 38.55 | 100.49 | 3.06 |
| VI. | 53.24 | 14.40 | 13.83 | 18.53 | 100.00 | 3.01 |

L. J. S.

Formation of Oceanic Salt Deposits. XXXIV. Maximal Tension of Constant Solutions at 83°. JACOBUS H. VAN'T HOFF, U. GRASSI, and R. B. DENISON (*Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 14, 518—521).—At the highest temperature limit chosen, namely, 83°, kainite no longer separated from solution, but, in addition to rock salt, the following salts must be considered; sylvite, carnallite, bischofite, kieserite, loewite, vanthoffite, thenardite, glaserite, langbeinite. The paragenesis of these minerals is graphically depicted. The quantitative relationships were experimentally studied by dilatometric methods conducted with the Bremer-Frowein tensimeter.

A. McK.

Formation of Oceanic Salt Deposits. XXXV. Composition of the Constant Solutions at 83°. JACOBUS H. VAN'T HOFF, HANS SACHS, and OTTO BIACH (*Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 18, 576—586).—The composition of the constant solutions at 83° has now been determined (compare preceding abstract) by the following method. The solution, which was almost saturated, was agitated at 83° with the powdered solid phases until the percentage of chlorine was constant; a further amount of solid was then added until the percentage of chlorine in the solution was unchanged, when the solid phase was analysed. The following solutions were examined: solutions of magnesium chloride, saturated with (a) sodium chloride, (b) sodium chloride and carnallite, (c) kieserite, (d) sodium chloride, carnallite, and kieserite respectively. Congruent solutions of the following combinations were next studied, namely, (1) sodium chloride and sodium sulphate, (2) sodium chloride and potassium chloride, (3) sodium chloride, potassium chloride and glaserite, (4) sodium chloride, glaserite and sodium sulphate, (5) sodium chloride, vanthoffite

and sodium sulphate, (6) sodium chloride, vanthoffite and loeweite, (7) sodium chloride, kieserite and loeweite, (8) sodium chloride, potassium chloride and carnallite. The remaining combinations were examined, namely, (1) sodium chloride, carnallite, kieserite and potassium chloride, (2) sodium chloride, potassium chloride, kieserite and langbeinite, (3) sodium chloride, kieserite, loeweite and langbeinite, (4) sodium chloride, potassium chloride, glaserite and langbeinite, (5) sodium chloride, glaserite, thenardite and vanthoffite, (6) sodium chloride, loeweite, glaserite and langbeinite, and (7) sodium chloride, loeweite, glaserite and vanthoffite.

The results are tabulated and graphically represented by a space diagram. A. McK.

Monazite in Sands from New South Wales. JOHN C. H. MINGAYE (*Records Geol. Survey, New South Wales*, 1903, 7, 222—226).—The sands of the Richmond river contain quartz, zircon, and ilmenite, with small amounts of cassiterite, platinum, iridosmine and gold. The following analysis of a highly concentrated sample from Broken Head, Ballina, shows that monazite is also present.

| P ₂ O ₅ . | Ce ₂ O ₃ . | (La, Di) ₂ O ₃ . | Y ₂ O ₃ . | ThO ₂ . | SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | CaO. |
|---------------------------------|----------------------------------|--|---------------------------------|---------------------------|--------------------|----------------------------------|----------------------------------|---------|
| 18.91 | 22.57 | 22.87 | 0.16 | 0.51 | 6.68 | 0.16 | 2.02 | 1.36 |
| ZrO ₂ . | SnO ₂ . | Ta ₂ O ₅ . | H ₂ O. | Au, Pt, Ir, Os, MnO, MgO. | | | Total. | Sp. gr. |
| 15.40 | 9.08 | 0.98 | 0.11 | traces | | | 100.81 | 5.224 |

L. J. S.

Wolframite from the Black Hills, South Dakota. J. D. IRVING (*Trans. Amer. Inst. Mining Engin.*, 1902, 31, (1901), 683—695).—Compact, black wolframite has recently been mined in the neighbourhood of Lead City. Analysis, by W. F. Hillebrand, of the ore gave :

| SiO ₂ . | WO ₃ . | Fe ₂ O ₃ . | FeO. | Al ₂ O ₃ . | MnO. | CaO. | SiO. |
|--------------------|-------------------|----------------------------------|----------------------------------|----------------------------------|---------------------------------|-------|--------|
| 12.87 | 61.50 | 3.85 | 9.18 | 0.52 | 8.21 | 0.93 | 0.02 |
| BaO. | Alkalis. | H ₂ O. | As ₂ O ₅ . | P ₂ O ₅ . | V ₂ O ₅ . | S. | Total. |
| 0.04 | 0.08 | 1.07 | 1.25 | 0.12 | trace | trace | 99.64 |

L. J. S.

Stolzite and Scheelite from Brazil. WILHELM FLORENCE (*Centr. Min.*, 1903, 725—728).—Stolzite, as thick-tabular, sulphur-yellow to orange-red crystals (analysis I), and scheelite, as pyramidal crystals and irregular, yellowish-grey grains (analysis II), occur with limonite and native gold in quartzite at Marianna, at the base of Mt. Itacolumi in Minas Geraes.

| | WO ₃ . | PbO. | CaO. | MgO. | Fe ₂ O ₃ , Al ₂ O ₃ . | Total. | Sp. gr. |
|-----|-------------------|-------|-------|------|---|--------|---------|
| I. | 50.92 | 47.78 | 0.92 | 0.19 | 0.03 | 100.11 | 8.305 |
| II. | 79.75 | — | 19.84 | 0.02 | — | 99.61 | 5.896 |

The reactions and microscopic crystals obtained with these minerals in blowpipe beads by the author's method (*Abstr.*, 1899, ii, 51) are described. L. J. S.

Chemical Composition of an American Modification of Gadolinite and Inclusions in it. G. P. TSCHERNIK (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 287—301).—The author gives the following analyses of specimens of gadolinite, of which I was found in Idaho, II represents inclusions in I, whilst III came from Ytterbia.

| | BeO. | FeO. | MgO. | CaO. | SiO ₂ . | ThO ₂ . | Y ₂ O ₃ . | Ce ₂ O ₃ . |
|------|------|-------|-------|------|--------------------|--------------------|---------------------------------|----------------------------------|
| I. | 9.98 | 12.74 | 0.21 | 0.60 | 24.41 | 0.30 | 42.94 | 1.94 |
| II. | 0.54 | 1.58 | trace | 0.62 | 26.08 | 2.77 | 51.94 | 14.49 |
| III. | 1.03 | 12.99 | 0.65 | 0.62 | 28.87 | trace | 48.32 | 2.48 |

| | (La, Pr, Nd) ₂ O ₃ . | Al ₂ O ₃ . | K ₂ O. | Na ₂ O. | H ₂ O. | MnO. | Total. | Sp. gr. |
|------|--|----------------------------------|-------------------|--------------------|-------------------|-------|--------|---------|
| I. | 5.52 | trace | trace | trace | 0.48 | — | 99.12 | 4.382 |
| II. | — | — | trace | trace | 0.97 | trace | 98.99 | 4.536 |
| III. | 4.91 | trace | trace | trace | 0.39 | — | 100.26 | 4.223 |

II may be expressed by the formula: $16[\text{Y}_2\text{O}_3, 2\text{SiO}_2] + 2[2\text{Ce}_2\text{O}_3, 3\text{SiO}_2] + \text{ThSiO}_4 + \text{BeSiO}_4 + 2\text{FeO} + \text{CaO} + 5\text{H}_2\text{O}$. The author gives a table of the analyses, by other authors, of gadolinites.
T. H. P.

Anthophyllite from Bohemia. V. ROSICKÝ (*Jahrb. Min.*, 1903, ii, Ref. 23; from *Abh. böhm. Akad. Wiss.*, 1902, No. 19, 1—7).—A white, fibrous mineral, proved by its optical characters and the following analysis, by H. Němeček, fills crevices and surrounds nodules in serpentine at Štříbrné Horky near Deutschbrod.

| SiO ₂ . | Al ₂ O ₃ . | Cr ₂ O ₃ . | FeO. | MnO. | NiO, CoO. |
|--------------------|----------------------------------|----------------------------------|------|------|-----------|
| 57.19 | 0.92 | 0.12 | 7.98 | 0.28 | traces |

| CaO. | MgO. | Na ₂ O. | H ₂ O (hygros.). | Loss on ignition. | Total. |
|------|-------|--------------------|-----------------------------|-------------------|--------|
| 0.76 | 28.03 | trace | 0.48 | 3.82 | 99.59 |

L. J. S.

Regular Intergrowth of Nemaphyllite and Dolomite from the Tyrol. FRIEDRICH FOCKE (*Tsch. Min. Mitt.*, 1902, 21, 323—345).—Associated with dolomite and chlorite at the Wildkreuzjoch, Zillertal, is a chlorite-like mineral, occurring as green scales with a fibrous structure, to which the name *nemaphyllite* is given. H. 3; sp. gr. 2.60. There is a good cleavage parallel to the base, nearly perpendicular to which emerges an acute negative bisectrix, the optic axial plane being parallel to the fibres constituting the plate. Analysis, by R. von Zeyneck, shows the mineral to have the composition of serpentine ($\text{H}_4\text{Mg}_3\text{Si}_2\text{O}_9$), from the antigorite, metaxite, and other varieties of which it differs in its structure.

| SiO ₂ . | Al ₂ O ₃ . | FeO. | MgO. | CaO. | Na ₂ O. | Mn, K. | H ₂ O. | Total. |
|--------------------|----------------------------------|------|-------|------|--------------------|--------|-------------------|--------|
| 42.49 | 0.40 | 4.63 | 37.60 | 0.72 | 2.11 | traces | 13.11 | 101.06 |

Nemaphyllite also occurs intimately and regularly intergrown with crystals of dolomite in such a manner that the plates and fibres of the

former are respectively parallel to the rhombohedral planes and edges of the latter. An analysis of the mixture shows the presence of 36 per cent. of nemaphyllite and 64 of dolomite. L. J. S.

Californian Minerals. WALTER C. BLASDALE (*Bull. Dep. Geol. Univ. California*, 1901, 2, 327—348).—Descriptions are given of various minerals from the crystalline schists and serpentine of the Berkeley Hills, near San Francisco, namely: actinolite (analyses I, II), glaucophane (III, IV), tremolite (V), prochlorite (VI, VII), talc (VIII), diallage (IX), altered diopside (X), serpentinised anthophyllite (XI), and albite (XII).

| | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | FeO | CaO | MgO | Na ₂ O | K ₂ O | H ₂ O (100°) | H ₂ O (>100°) | TiO ₂ | MnO | Total |
|-------|------------------|--------------------------------|--------------------------------|-------|-------|-------|-------------------|------------------|----------------------------|-----------------------------|------------------|-------|--------|
| I. | 55·21 | 3·45 | — | 7·49 | 10·50 | 18·97 | 2·45 | — | — | 1·75 | — | — | 99·82 |
| II. | 55·56 | 2·05 | — | 5·97 | 12·13 | 19·45 | 1·94 | 0·30 | — | 2·58 | — | — | 99·98 |
| III. | 54·52 | 5·25 | 4·44 | 9·81 | 1·98 | 10·33 | 7·56 | 0·16 | — | 1·78 | 0·39 | 0·46 | 100·68 |
| IV. | 52·39 | 11·29 | 3·74 | 9·13 | 3·03 | 11·27 | 6·14 | trace | — | 2·57 | 0·14 | trace | 99·80 |
| V. | 56·68 | 1·79 | 1·70 | 2·23 | 15·80 | 19·35 | — | — | 0·10 | 2·25 | — | — | 99·90 |
| VI. | 27·38 | 26·15 | 0·78 | 12·70 | — | 18·92 | 1·15 | — | 1·51 | 11·44 | — | — | 100·03 |
| VII. | 27·03 | 20·07 | 4·72 | 16·47 | — | 18·90 | 0·72 | 1·22 | — | 11·78 | — | — | 100·91 |
| VIII. | 56·02 | 9·02 | 1·10 | 5·14 | 0·60 | 24·10 | — | — | 0·16 | 4·34 | — | — | 100·48 |
| IX. | 51·91 | 3·55 | 1·30 | 2·65 | 22·85 | 16·15 | 0·56 | — | 0·21 | 0·86 | 0·10 | 0·33 | 100·47 |
| X. | 49·62 | 2·97 | 2·49 | 2·99 | 19·14 | 19·72 | 0·60 | — | — | 2·71 | — | — | 100·24 |
| XI. | 67·09 | 20·47 | — | — | 0·24 | — | 10·96 | — | 0·27 | 0·59 | — | — | 99·62 |

L. J. S.

Gismondite from Silesia. ARTHUR SACHS (*Centr. Min.*, 1904, 215—216).—Analysis of gismondite from the basalt of Nicolstadt, near Liegnitz, gave the following results, agreeing with the formula $(Ca, Na_2, K_2)Al_2Si_2O_8 \cdot 4H_2O$, which is the same as that recently proposed for this mineral by Zambonini (*Abstr.*, 1903, ii, 656).

| SiO ₂ | Al ₂ O ₃ | CaO | K ₂ O | Na ₂ O | H ₂ O | Total |
|------------------|--------------------------------|-------|------------------|-------------------|------------------|--------|
| 34·19 | 28·34 | 13·15 | 2·35 | 1·82 | 20·41 | 100·26 |

L. J. S.

Wolchonskoite from Russia. PETR IVANOVICH KROTOV (*Jahrb. Min.*, 1903, ii, Ref. 177; from *Tageb. XI Vers. russ. Naturf.*, 1901, No. 4, 123—133; *Verh. russ. min. Ges.*, 1902, 40, 1—11).—Wolchonskoite, similar in appearance to that of Ochansk, Siberia, occurs in a calcareous sandstone of Permian age at Uchtym, gov. Viatka, Russia. Under the microscope, it is seen to be finely fibrous and birefringent. Analysis, by Karpov, gave:

| SiO ₂ | Cr ₂ O ₃ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | H ₂ O (comb.) | H ₂ O (hygros.) | Total |
|------------------|--------------------------------|--------------------------------|--------------------------------|------|------|-----------------------------|-------------------------------|--------|
| 42·30 | 19·34 | 4·38 | 2·21 | 4·92 | 1·60 | 7·36 | 18·18 | 100·29 |

Formula, $2(Ca, Mg)(Cr, Al, Fe)Si_{10}O_{25} \cdot 6H_2O$.

L. J. S.

Occurrence of Vanadium in New South Wales Rocks, Coals, Clays, &c. JOHN C. H. MINGAYE (*Records Geol. Survey, New South Wales*, 1903, 7, 217—221).—Vanadium, varying from traces to the following maximum amounts, was found: basalt, 0·06 per cent.

V_2O_5 ; coal, 0.12; bog-head mineral ("kerosene shale"), 0.05; white clay, 0.08. Bricks manufactured from this vanadiferous clay, when exposed to the weather, become stained yellowish-green and red; the colouring matter of the stains is soluble in water, and consists mainly of potassium vanadate.

In Scotch oil-bearing shales was found a maximum of 0.12 per cent. V_2O_5 .

An analysis is also given of montanite (Abstr., 1903, ii, 489).

L. J. S.

Physiological Chemistry.

Studies in Body Temperature. I. Influence of Inversion of the Daily Routine. FRANCIS G. BENEDICT (*Amer. J. Physiol.*, 1904, 11, 145—169).—No tendency to an inversion of the daily temperature curve by inverting the routine of life is observed in any of the experiments here recorded. This is opposed to what is usually stated, but in the present experiments on night workers, the observations lasted over a considerable time, and appear to have been made with great care and assiduity. Due allowance is made for the influence of muscular work in raising the body temperature temporarily.

W. D. H.

Relation of Oxygen and Hæmoglobin. CHRISTIAN BOHR (*Chem. Centr.*, 1904, i, 902—903; from *Centr. Physiol.*, 17, 682—688; 688—691).—The following equation is stated to represent the relationships of oxygen and hæmoglobin:

$$K.C.y^2\left(1 + \frac{k}{x^2}\right) = x^2\left(\frac{B}{y}\right) \div yk.$$

y = c.c. of oxygen which unites with 1 gram of hæmoglobin at x tension.

B = c.c. of oxygen which 1 gram of hæmoglobin is capable of uniting with in maximum.

C = concentration of hæmoglobin solution.

K and k are constants.

The results obtained with hæmoglobin solutions correspond well with those calculated from this formula. In the blood at 150 mm. pressure, the results coincide with those obtained with solutions of hæmoglobin. At lower pressures, the amount of oxygen is smaller with hæmoglobin solutions than in the blood. The name hæmochrome is suggested for the blood pigment; this is probably not the same thing as pure hæmoglobin. In different preparations, the yield of globin differs; possibly also the pigment is united to alkali, and to lecithin in the corpuscles.

W. D. H.

Variations in Respiration and Blood Pressure produced by Propeptone in Dogs. PIERRE NOLF (*Bull. Acad. roy. Belg.*, 1904, (ii), 147—153).—Injection of propeptone (proteoses) into the dog's circulation causes the appearance of periodicity in respiration and arterial pressure. This is not the effect of the material injected on the bulbar centres, for similar effects can be produced by any kind of agitation (sensory or painful) in non-anæsthetised animals. The injection of propeptone is simply one means of calling forth these responses, although the variations are usually more regular on account of the diminution of tonus, both in the peripheral vessels and in the action of the vagus, which follows the injection.

W. D. H.

A Perfusion Stopcock. FRANK S. LOCKE (*Proc. physiol. Soc.*, 1904, xii—xiii; *J. Physiol.*, 31). **Action of Dextrose on the Isolated Mammalian Heart.** FRANK S. LOCKE (*ibid.*, xiii—xiv). **Action of other Sugars on the Isolated Mammalian Heart.** FRANK S. LOCKE and OTTO ROSENHEIM (*ibid.*, xiv). **Disappearance of Dextrose when Perfused through the Isolated Mammalian Heart.** FRANK S. LOCKE and OTTO ROSENHEIM (*ibid.*, xiv—xv).—A continuation of previous work on the perfusion of the mammalian heart, including the description of improvements in apparatus. The favouring action of dextrose can be obtained with solutions containing as little as 1 part of dextrose in 100,000 of Ringer's solution. The latent period of 1 to 0.1 per cent. solutions is at most 2—3 seconds. Galactose, rhamnose, L-arabinose, and glucoheptose are inactive. Perfusion of 0.1 to 0.25 per cent. solutions of dextrose for 7—10 hours through a rabbit's heart (weighing 5—6 grams) causes the disappearance of from 5 to 9 centigrams of dextrose. No glycolytic ferment is found in the fluid; disaccharides and lactic acid were not found.

W. D. H.

Formation of Glycuronic Acid in the Blood. RAPHAEL LÉPINE and BOULUD (*Compt. rend.*, 1904, 138, 610—614. Compare Abstr., 1902, ii, 619).—The liver contains glycuronic acid; it is the presence of combinations of this acid to which is attributable the lævorotatory power of blood drawn from the hepatic vein. There is also more glycuronic acid in venous blood generally than in arterial blood.

W. D. H.

The Rennin Action of Blood Serum. IVAR BANG (*Beitr. chem. Physiol. Path.*, 1904, 5, 395—396).—The statement was made by Fuld and Spiro (Abstr., 1901, ii, 67), that the rennin-like action of blood is due to euglobulin, and the antirennin to pseudo-globulin. In the present paper, the opinion is advanced that euglobulin, when precipitated, simply carries down the ferment with it.

W. D. H.

Action of Concentrated Electric Light and Radium Emanations on Rennin (Chymosin) Renninogen and Anti-rennin. SIGVAL SCHMIDT-NIELSEN (*Beitr. chem. Physiol. Path.*, 1904, 5, 355—376, 398—400).—The time taken to curdle milk is the

measure adopted for the activity of the ferment. The action of the substances named is markedly hindered by the ultra-violet rays of electric light. The action of radium emanations is minimal. Thus, in the two experiments cited, the coagulation time of milk was lengthened from $7\frac{1}{2}$ to 9, and from 9 to 10 minutes respectively. W. D. H.

The Origin of Precipitins. R. KRAUS and C. LEVADITI (*Compt. rend.*, 1904, 138, 865—866).—Reasons are given for the view that the precipitins originate from the leucocytes, or at any rate that they are principally derived from these cells. W. D. H.

Absorption through the Skin. SCHWENKENBECHER (*Chem. Centr.*, 1904, i, 1020; from *Arch. Anat. Physiol., physiol. Abth.*, 1904, 121—165).—By admixture with oily materials, many substances are absorbed through the skin; a long list of these is given, which includes alcohol, chloroform, various cyanides, acetone, phenol, salicylic acid, antipyrin, potassium iodide. Strychnine, coniine, carbon monoxide, coal-gas, lithium chloride were not absorbed. The absorbed substances were detected either by their physiological effects, or their subsequent appearance in the urine. Salts such as potassium cyanide were not absorbed as such, but dissociation occurred in the outer skin layers owing to high tension of carbon dioxide. In the case of some salts, absorption of only one constituent occurred; for instance, with lithium salicylate, salicylic acid was absorbed, and lithium not.

W. D. H.

Influence of Thiocyanates on Metabolism. The Amount of Thiocyanate in Saliva and Urine. ARTHUR MAYER (*Chem. Centr.*, 1904, i, 824; from *Arch. klin. Med.*, 79, 194—208, 209—214).—On giving thiocyanates by the mouth, the excretion of thiocyanogen is largely augmented; the oxidation of proteid is diminished, and the amount of unoxidised sulphur compounds in the excretions increased. This agrees with the action of other cyanogen compounds; in particular, hydrogen cyanide lessens oxidative processes.

In regard to the amount of thiocyanate in the saliva and urine of healthy persons, the following numbers are given. A healthy man excretes in the urine an average of 0.0476 gram daily; in women the amount is less. In saliva, the amount is 0.003 gram per litre. Tobacco-smoking, muscular exercise, and fever increase the amount in the urine. The amount in the saliva runs parallel, although the substance in the saliva is not the only source of the urinary thiocyanate.

W. D. H.

Formation of Sugar from Fat. EMIL ABDERHALDEN and PETER RONA (*Zeit. physiol. Chem.*, 1904, 41, 303—307).—Finely-minced liver was divided into two portions, one of which was mixed with olive oil, or oleic acid, and blood; the other with blood only. After 5 or 6 hours, the amount of sugar in the different portions was estimated, but the differences found were always within the limits of experi-

mental error, sometimes in one, sometimes in the other direction. These observations, therefore, yield no support to Seegen's view of the formation of carbohydrate from fat in the liver. W. D. H.

The Origin of Lactose. CH. PORCHER (*Compt. rend.*, 1904, 138, 833—836; CH. PORCHER and COMMANDEUR (*ibid.*, 862—865).—In experiments on pregnant goats from which the mammary glands had been removed, it was found that after delivery dextrose appeared in blood in excess and also in the urine. The conclusion is drawn that the mammary tissue is able in normal circumstances to transform the glucose of the blood into lactose and excrete it. The urinary sugar does not come from the hydrolysis of lactose, because galactose is absent from the urine of these animals. Observations on the urine of women confirm this view. W. D. H.

Influence of Food on Milk Secretion and on the Composition of Milk. GUSTAV FINGERLING (*J. Landw.*, 1904, 52, 147—149).—Referring to the investigations of Lemmermann and Linkh (*Landw. Jahrb.*, 32, 559), the object of which was to avoid the use of stimulants in the basal ration, it is pointed out that the substances employed (lucerne and mangels) are both stimulants. Addition of hay distillate to a food containing no stimulant improves both the yield and quality of milk. The same result is obtained by adding fenugreek to hay which has been rained upon. N. H. J. M.

Action of Formaldehyde on Milk. AUGUSTE TRILLAT (*Compt. rend.*, 1904, 138, 720—722).—The employment of formaldehyde is shown to render more or less of the casein of milk indigestible. A further objection to its use is that nearly the whole of the formaldehyde remains unchanged, and, being absorbed by the system, may act injuriously on digestion. N. H. J. M.

Adaptation of the Pancreas. F. A. BAINBRIDGE (*J. Physiol.*, 1904, 31, 98—122).—The dog's pancreas normally contains no lactase, although this enzyme is present in extracts of the intestinal mucous membrane. But, as Weinland showed, when dogs are kept on milk diet for two weeks, their pancreatic juice obtained by secretin always contains lactase. This occurs only when lactose is given by the mouth, not when it is injected subcutaneously; it represents a definite adaptation of the pancreas to diet. Subcutaneous injections of extracts of intestinal mucosa of biscuit-fed dogs do not, but of milk-fed dogs do, cause the appearance of lactase in the pancreatic juice. The pancreas of new-born puppies secretes no lactase; this enzyme appears within a few days. The adaptation described is due to a chemical mechanism; lactose acts on the intestinal mucosa so as to produce some substance which is carried in the blood to the pancreas, which is thus stimulated to produce lactase. Secretin is not modified by diet; it excites the secretion of all the enzymes present in the pancreas at the time. W. D. H.

2-cyclohexanone has been effected. 1-Methylcyclohexanone was obtained from a tetrahydrotoluene, an account of which has previously been given (Abstr., 1902, i, 750). The *nitrosate* of tetrahydrotoluene crystallises in needles melting at 107—108°. When the hydrocarbon is oxidised at 0° by one per cent. permanganate, δ -acetylvaleric acid is obtained, and can be isolated as the semicarbazone (m. p. 144—146°); the hydrocarbon must therefore be represented by the formula $\text{CH}_2 < \begin{smallmatrix} \text{CH}_2 - \text{CH} \\ \text{CH}_3 \cdot \text{CH}_2 \end{smallmatrix} > \text{CMe}$, and is probably identical with the hydrocarbon (b. p. 108°) obtained by Markownikoff (Abstr., 1900, i, 579) and called "a-naphthylene."

When the nitrosate is warmed with sodium methoxide, an *oxime* is obtained, which forms crystals melting at 40—42°, and boils at 115—117° under 11 mm. pressure (compare *loc. cit.*). It yields two benzoyl derivatives, an *a-compound*, which crystallises in needles melting at 142—143°, and is sparingly soluble in ether, and a *β -compound* melting at 90—91° and readily soluble in ether. On boiling the oxime with hydroxylamine hydrochloride, it undergoes an isomeric change into an *oxime* which melts at 62—63°, and yields a *benzoyl* derivative melting at 142—143°. By warming with sulphuric acid, both oximes are converted into methylcyclohexenone, the sp. gr. of which is now given as 0.9680, and the n_D as 1.4831 at 20° (compare *loc. cit.*). The *semicarbazone* melts at 207—208°.

1:2-Methylcyclohexanol, $\text{C}_7\text{H}_{13}\cdot\text{OH}$, prepared by reducing the methylcyclohexenone by sodium and alcohol (Abstr., 1902, i, 801), boils at 168—170° and has a sp. gr. 0.921 and n_D 1.4696; the *phenylurethane* obtained from it melts at 103—104°.

The methylcyclohexanol is oxidised by chromic acid to 1:2-methylcyclohexanone, which was found to be identical with the compound synthesised from methyladipic acid by Zelinsky and Generoso (Abstr., 1896, i, 350); it has n_D 1.4461 at 21.5°, and forms an *oxime* melting at 43—44°, the *benzoyl* derivative of which melts at 70—72°. When oxidised by chromic acid in the presence of dilute sulphuric acid, δ -acetylvaleric acid is formed; its constitution was fixed by oxidising it to adipic acid by means of sodium hypobromite. K. J. P. O.

Preparation of ψ -Ionone. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 147839).—In the preparation of ψ -ionone by the condensation of citral with acetone, the yield is considerably improved when the reaction is carried out in the absence of water. Sodamide or potassamide is employed as a condensing agent, and benzene is added, if necessary, to dilute the reacting substances. C. H. D.

Action of Phosphorus Pentasulphide on Benzophenone-oxime. R. CIUSA (*Gazzetta*, 1904, 34, i, 102—104).—Phosphorus pentasulphide reacts explosively with benzophenoneoxime at 80°; in boiling carbon disulphide solution, the action takes place smoothly, a *substance*, $\text{C}_{10}\text{H}_{10}\text{O}_3\text{S}$, being formed, which crystallises from aqueous alcohol in plates, melts at 86°, and, on reduction with zinc and hydrochloric acid, evolves hydrogen sulphide. W. A. D.

and ammonium sulphate. The failure of some observers to find arginine in the products of auto-digestion of organs is doubtless due to the previously unsuspected action of arginase, which must be now placed among Richet's urea-forming ferments. W. D. H.

Effect of Raw Meat Diet on Fowls. CHALMERS WATSON (*Proc. physiol. Soc.*, 1904, v—vi; *J. Physiol.*, 31).—Fowls fed only on raw meat and water succumb at periods from 3 to 16 months, the terminal symptoms being paralytic; the thyroid and parathyroid glands are enormously enlarged. One exception to this rule was noted, and the animal gained weight; after death, it was found to be tubercular.

W. D. H.

Relations between Food Fat, Body Fat, and Milk Fat. ALBERT EINECKE (*Bied. Centr.*, 1904, 33, 239—245; from *Inaug. Diss. Breslau*, 1903).—The results of experiments with goats indicate that with liberal and comprehensive rations the yield of milk and fat depends only on the individuality of the animal. There seems to be no direct migration of food fat to the milk, although the food fat is undoubtedly utilised in the production of milk fat. The slow and slight changes in the Reichert-Meissl numbers indicate other sources for milk fat production, such as carbohydrates and proteids.

N. H. J. M.

Rhythm of Strips of Heart Muscle. E. G. MARTIN (*Amer. J. Physiol.*, 1904, 11, 103—138).—Isolated strips of turtle's heart contain all the conditions essential for rhythmic action, provided they are brought into play. Immersion in 0·7 per cent. sodium chloride solution induces spontaneous beats, but these do not continue long unless calcium is also present. Smaller amounts of sodium chloride are effective if the solution is kept isotonic by an indifferent substance like cane-sugar. Many other details concerning the action of various salts and the means of inducing recovery after standstill, and a theoretical discussion of the results, are given.

W. D. H.

Lymphatic Organs. IV. IVAR BANG (*Beitr. chem. Physiol. Path.*, 1904, 5, 317—320).—The cells of the lymph glands and their nucleate dissolve in physiological saline solution. Thymus cells are unaltered by 0·7 per cent. solution of sodium chloride, but dissolve in distilled water. The nucleate they contain is soluble in distilled water and precipitated by 0·7 per cent. sodium chloride. The red corpuscles of the goose are almost insoluble in water, and their nucleate is precipitated by minimal amounts of sodium chloride. It is difficult to extract all the salt from these corpuscles, and the residue probably hinders the dissociation and solution of the nucleate. These observations support the author's previous views on the importance of nucleate in the constitution of cells.

W. D. H.

[Arsenic in Lower Animals]. WALTHER HAUSMANN (*Beitr. chem. Physiol. Path.*, 1904, 5, 397—398).—In sea water containing a small quantity of arsenious acid, the action in *Aiptasia diaphana* forms an

unpleasant-smelling gas, indicating the formation of arsines from the acid. This action, however, is mainly attributed to a certain yellow symbiotic alga.
W. D. H.

Occurrence of Ethereal Sulphates, Taurine, and Glycine in Lower Animals. AGNES KELLY (*Beitr. chem. Physiol. Path.*, 1904, 5, 377—383).—The occurrence of ethereal sulphates in the skeletal structures of invertebrates has been previously noted. In the present research, none was found in *Tubularia*, *Sertularella*, *Alcyonium*, *Cellaria*, the byssus of *Mytilus edulis* and the head cartilage of sepia. Positive results were obtained among echinoderms, especially in the skin of *Stichopus regalis*. Taurine was obtained from the muscles and organs of Bojanus of *Mytilus*, and is regarded as a direct decomposition product of proteid; glycine could not with certainty be determined here; the organ of Bojanus contains a large amount of fermentable sugar. Glycine was found by Chittenden in the muscles of *Pecten irradians*; it is still more abundant in those of *P. opercularis*.
W. D. H.

Glycogen of the Fœtal Liver. EDUARD PFLÜGER (*Pflüger's Archiv*, 1904, 102, 305—319).—The new method of estimating glycogen has shown there is no foundation for the statement that in early periods of fetal life the liver contains no glycogen, although whether it is richer in that substance in the later periods is not yet settled. Details are given of the dissociation and reassociation of the iodide of glycogen, and also of the means of avoiding admixtures which are present in glycogen as precipitated from liver and muscles of adult animals by means of strong potassium hydroxide. Such contaminations interfere with the iodine reaction.
W. D. H.

Removal of the Amino-group (Desamidierung) in the Animal Body. S. LANG (*Beitr. chem. Physiol. Path.*, 1904, 5, 321—345).—This question is one of great importance in the study of nitrogenous metabolism. Several previous observers have found ferments capable of splitting off nitrogen from amino-compounds. In the present research, the finely-divided fresh tissue was mixed with an amino-substance, and the ammonia formed was estimated. Antisepsis was maintained with toluene. It is shown how widespread such an action is; it will possibly explain the formation also of such substances as fat and carbohydrate from the non-nitrogenous residue. There are differences in different cases. Thus, glycine is easily decomposed, especially by the intestine and pancreas; the liver, kidney, suprarenal, and testis come next. It is unaffected by the spleen and lymph glands. Tyrosine is almost unaffected by the liver, but is decomposed by the suprarenal. Uric acid is affected by the liver, spleen, kidney, and intestine, but very little by muscle. The other substances investigated were phenylalanine, leucine, cystin, asparagine, glutamine, acetamide, urea, and glucosamine.
W. D. H.

Oxidation of Formic Acid by Extracts of Animal Tissues in the presence of Hydrogen Peroxide. F. BATTELLI (*Compt. rend.*, 1904, 138, 651—652).—In the presence of hydrogen peroxide, extracts of liver and muscle oxidise formic acid, with the formation of carbon dioxide. No similar oxidation was observed with sugar, oxalates, lactates, or acetates. The substance to which the oxidising action is due has the characters of an enzyme.

W. D. H.

The Bile Salts of Ox Bile. STEPHAN TENGSTROM (*Zeit. physiol. Chem.*, 1904, 41, 210—222).—As a preliminary to the study of the choleic acid compounds in bile, the present research relates to the fractional separation of sodium glycocholate and taurocholate. For this purpose, salts of the heavy metals were used, and different fractions analysed; as a rule, the glycocholate is more readily precipitable. The best results appear to have been obtained with a combination of potassium alum and ferric chloride; the final fraction contained 95.8 per cent. of taurocholate. Sodium chloride causes no precipitate in bile, the salting out of the taurocholate being hindered by the alkali salts present, but after the bile has been treated with lead acetate and ferric chloride and the filtrate freed from iron by sodium carbonate and neutralised with hydrochloric acid, saturation with sodium chloride then produces a precipitate containing 99.4 per cent. of taurocholate.

W. D. H.

Human Bladder Bile. TOKUYE KIMURA (*Chem. Centr.*, 1904, i, 1018—1019; from *Arch. klin. Med.*, 79, 274—289).—The bile was removed after death, and examined in relation to its colour, dry residue, density, and viscosity. Search was also made for urobilin and urobilinogen. Many biles contain the former pigment, and those which do not, contain its precursor. Urobilinogen was identified spectroscopically after removal of the ordinary bile pigment by precipitation with barium oxide; dimethylaminobenzaldehyde hydrochloride then gives a red colour with a typical absorption band in the orange. In order to detect urobilinogen in the faeces by this method, it is necessary first to remove indole and scatole with light petroleum. In addition to the known bile pigments, a brown one not identical with any previously known is described. In a case of obstructed bile duct, hæmatin was also present. The observations in various pathological conditions on bile viscosity are important from the point of view of the etiology of jaundice.

W. D. H.

Calorimetric Investigations of Fæces. HANS LOHRISCH (*Zeit. physiol. Chem.*, 1904, 41, 308—320).—The importance of a calorimetric examination of the fæces in metabolism experiments is admitted by all, and much of the present paper is concerned with the methods used. The results show that the heat-value of the fæces was always greater than that calculated from the composition. The excess has no regularity in its amount. This is attributed to errors in the chemical analysis; for instance, reckoning the lecithin and cholesterol in the ethereal extract as fat, and the difficulties of estimating correctly the numerous organic substances present.

W. D. H.

Chemistry of Malignant Growths. I. S. P. BEEBE (*Amer. J. Physiol.*, 1904, 11, 139—144).—In the present paper, the examination of four tumours (one cancer, two sarcomata, and one hypernephroma) was undertaken. The principal point of interest recorded is the presence of proteolytic autolysis (leucine, tyrosine, tryptophan, glycine, &c.). The tissue was sterile in each case. Fatty degeneration is believed to involve a kind of proteolysis. In one sarcoma, a substance like glycogen, but possibly with a larger molecule, was found.

W. D. H.

Action of Artificial Oxydases on Infectious Diseases. ALBERT ROBIN and G. BARDET (*Compt. rend.*, 1904, 138, 783—785).—The action of colloidal metals, especially manganese, in several infectious maladies is to promote oxidation in the tissues, and cure of the disease.

W. D. H.

Action of Artificial Oxydases on the Tetanus Toxin. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and J. CHEVROTIER (*Compt. rend.*, 1904, 138, 652—654).—Manganese salts in the presence of a colloid play the part of an oxydase (Trillat). The same is true for emulsions of iron oxide and cerium oxide. The action of these oxidising agents is to destroy the toxicity of tetanus toxin.

W. D. H.

Behaviour of Carbon Monoxide in the Organism. PIERO GIACOSA (*Atti R. Accad. Sci. Torino*, 1904, 39, 421—428).—About 66—70 per cent. of the total blood in the body of a dog was removed from the carotid artery and replaced, by transfusion through the jugular vein, by a somewhat larger quantity of blood which had been saturated with carbon monoxide. Beyond showing febrile tremors, an increased pulse-frequency, and copious diuresis, the condition of the animal was not greatly affected; after several hours, it was quite normal, and no ill-effects could be detected. Whilst its blood remained saturated with carbon monoxide, the dog could inhale with little inconvenience much larger quantities of the gas, mixed with air, than would be normally sufficient to cause death. From these results, the author considers that the usually accepted theory that carbon monoxide poisons by replacing the oxyhæmoglobin of the blood by carboxyhæmoglobin can no longer be admitted.

W. A. D.

The Part played by Benzene in Poisoning by Coal Gas. R. STAHELIN (*Proc. Roy. Soc.*, 1904, 73, 78—83).—Coal gas produces first excitation, then rigor of isolated frog's muscles. The excitatory phenomena in frogs are at rest in an atmosphere of carbon monoxide or nitrogen. The specific effects are produced by benzene in the gas, and can be brought about by air containing the same percentage of benzene; there is, however, no reason to suppose that the toxic effect of coal gas on mammals is determined by anything except its content of carbon monoxide.

W. D. H.

Effect of Sodium Hydroxide Solutions injected Intravascularly, and the Cause of Apnoea. ANTOINE HOUARDY (*Bull. Acad. roy. Belg.*, 1904, (ii), 123—146).—Intravascular injection of

sodium hydroxide increases the alkalinity of the blood, but in the dog this is frequently not apparent owing to the hæmoglobinuria produced. If, as is believed, the alkali fixes the carbon dioxide of the blood, it should lessen the tension of this gas in the blood, and thus, according to Fredericq's theory, produce apnœa. It was found that this is what does occur provided the injection is made rapidly. Section of the pneumogastric nerves does not modify the results.

W. D. H.

Action of Formic Acid on the Muscular System. E. CLÉMENT (*Compt. rend.*, 1904, 138, 785—787).—Forty drops of formic acid, neutralised by sodium hydrogen carbonate and taken in half a glass of water daily, increase the muscular force enormously as measured by the ergograph, and delay the onset of fatigue.

W. D. H.

Action of Formic Acid on the Organism. L. GARRIGUE (*Compt. rend.*, 1904, 138, 837).—In reference to Clément's work (preceding abstract), it is pointed out that from experiments on animals the invigorating action of formates had been previously demonstrated by the author (*Maladies microbiennes*, Paris, 1903).

W. D. H.

Histological Changes produced by the Injection of Adrenaline Chloride. W. B. DRUMMOND (*J. Physiol.*, 1904, 31, 82—91). **The Influence of Adrenaline Poisoning on the Liver.** W. B. DRUMMOND and D. NOËL PATON (*ibid.*, 92—97).—The histological changes produced by adrenaline are partly necrotic, as in the liver and kidney, and partly congestive, as in the lungs. They are due in part to the rise of blood pressure, and in part to a direct toxic action on the tissue cells. Degenerative changes are also seen in the blood vessels. The liver changes probably account for the fall of urea-nitrogen excreted. Brodie's contention that adrenaline is harmful in hæmoptysis is supported. In acute adrenaline poisoning, the degenerative changes in the liver are most marked in the centres of the lobules, and the amount of glycogen is lessened. In chronic poisoning, the amount of glycogen is not necessarily altered.

W. D. H.

Action of the Ileo-colic Sphincter. T. R. ELLIOT (*J. Physiol.*, 1904, 31, 157—168).—Anæmia and adrenaline produce the same effect as sympathetic stimulation, namely, constriction of this sphincter.

W. D. H.

Physiological Action of the Jaborandi Alkaloids. CHARLES R. MARSHALL (*J. Physiol.*, 1904, 31, 123—156).—Jaborandi leaves contain pilocarpine, isopilocarpine, and pilocarpidine. Merck's jaborine consists mainly of the two first, but contains in addition an alkaloid possessing an atropine-like action. The action of pilocarpine on the heart is almost exactly similar to that obtained by vagal stimulation. Small doses increase the sensitiveness of the vagus to electrical stimuli. Atropine counteracts an excessive amount of pilocarpine; 1 part of atropine in 1000 of pilocarpine can often be detected physiologically. *iso*Pilocarpine produces a much weaker, and pilocarpidine an even weaker, but similar, effect. The homopilopic

portion of the molecule acts as the haptophore group. Solutions containing the hydroxy-acid corresponding with lactone-pilocarpine are inactive. The influence of the glyoxaline part of the molecule has not yet been determined.

W. D. H.

Physiological Action of Lobeline. CHARLES W. EDMUNDS (*Amer. J. Physiol.*, 1904, 11, 79—102).—In frogs, lobeline causes first excitation, then depression of the central nervous system, with loss of reflexes and a curare-like action on the muscles. On cold-blooded hearts it acts like nicotine, and also inhibits the action of muscarine. In cats and dogs it is a powerful emetic, due to action on the vomiting centre. In larger doses there are muscular twitchings, convulsions, and finally death. In small doses it stimulates, in large doses paralyzes, the respiratory centre. Stimulation of the vagus has no effect on the bronchial muscles after lobeline (Dreser). The effects on blood pressure are all explicable on the hypothesis that the drug first stimulates, then depresses, sympathetic ganglia, especially the superior cervical, vagus, and renal ganglia. Tolerance to the drug was not observed in cats.

W. D. H.

Influence of Morphine on the Movements of the Alimentary Canal in Rabbits during Inanition. N. W. KRYLOFF (*Pflüger's Archiv*, 1904, 102, 287—304).—In continuation of previous work by Swirski (*Arch. exp. Path. Pharm.*, 1902, 48, 282), it is shown that in normal rabbits the contents of the stomach and cæcum are about equal in quantity. In inanition of about 4 days, the stomach more or less empties itself, especially if the animal is muzzled, and excess of material is found in the cæcum. If morphine is given, either by the mouth or subcutaneously, the nervous control of peristalsis is weakened, and the contents of the stomach are greater whether the animal is muzzled or not, and the relationship between them and the contents of the cæcum approaches the normal.

W. D. H.

Lecithin and Snake Poison. PRESTON KYES (*Zeit. physiol. Chem.*, 1904, 41, 273—277).—Lecithin is the activator for the amboceptor of snake venom; the greater toxicity and hæmolytic action of cobra venom on foetal ox blood as compared to that of the fully grown ox, is due to the more loosely bound condition of the lecithin in the red corpuscles in the former case. The same explanation is adopted for the greater hæmolytic action exhibited towards the blood of certain classes of animals. The addition of lecithin to the more resistant kinds of blood renders them susceptible to the toxic action of the venom. The venom of several kinds of snakes was investigated. The protective action of Calmette's serum is related in a corresponding way to the avidity of the toxins for lecithin.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Action of Oxidising Agents on the Purity of Industrial Fermentations. HENRI ALLIOT and GILBERT GIMEL (*Compt. rend.*, 1904, 138, 911—913).—The authors find that such oxidising agents as sodium or calcium hypochlorite, ferric chloride, potassium perchlorate or chlorate, or dichromate, manganese dioxide, or hydrogen peroxide have an inhibiting effect on the development of the butyric ferment, hydrogen peroxide, calcium hypochlorite, and manganese dioxide being the most effective in this respect; for this reason, and also because they accelerate the growth of the yeast cells, the presence of oxidising agents during the process of alcoholic fermentation is to be recommended.
M. A. W.

Fruit-ether Formation in Alcoholic Fermentation. THOMAS BOKORNY (*Chem. Zeit.*, 1904, 28, 301—302).—Fruit-ether formation during the fermentation of sugars into alcohol and carbon dioxide, that is, the formation of aliphatic esters with an aromatic odour or of aldehydes with an agreeable odour, is not occasioned by a special enzyme. Fruit-ether formation is invariably dependent on the presence of a fermentable sugar.
A. McK.

Action of Trimethylxanthine on Bacterium Typhi and B. Coli. EMIL ROTH (*Arch. Hygiene*, 1904, 49, 199—228).—The development of *Bacterium coli* may be completely checked by addition of certain amounts of caffeine, whilst *B. typhi* is very slightly, if at all, affected.
N. H. J. M.

Amide-splitting Ferments in Fungi. K. SHIBATA (*Beitr. chem. Physiol. Path.*, 1904, 5, 384—394).—The mycelium of *Aspergillus niger* contains an enzyme or a group of enzymes which are capable of splitting off ammonia from urea, biuret, and certain amino-acids. The term *amidase* is suggested. No tyrosinase was discovered.
W. D. H.

Germination of Barley. ARVID NILSON (*J. Amer. Chem. Soc.*, 1904, 26, 289—294).—The author considers that the chemical changes which constitute the germination of barley are induced by lactic acid bacteria, and has obtained indications that the acid produces the enzyme from the insoluble protein molecule. Substances injurious to the enzymes do not hinder the growth of barley if the injurious influence can be neutralised by the action of the bacteria. If, however, the bacteria are destroyed without injuring the enzymes, germination is checked for a time.

In addition to lactic acid bacteria, barley contains ammonia-producing bacteria. The presence of the latter accounts for the fact that barley steeped in dilute ammonia will decay, but not grow.

N. H. J. M.

Development of Annual Fatty Plants. Study of the Nitrogen and Ternary Substances. GUSTAVE ANDRÉ (*Compt. rend.*, 1904, 138, 639—644. Compare this vol., ii, 200).—The relation of phosphoric acid to nitrogen is highest at the end of the flowering period. The variations in the relation of amide to total nitrogen are slight during the whole period of the growth of *Mesembrianthemum crystallinum*, but were more in the case of the two other plants (*loc. cit.*). Nitrates were found at all times, diminishing in quantity during the period of growth, and increasing when no longer required for the production of proteids.

The amount of water-soluble carbohydrates were found to be high during the whole period as compared with the saccharifiable carbohydrates. It is suggested that a transformation of acids into carbohydrates goes on in the daytime, the reverse taking place in the night.

The amount of vasculin differs in the three plants, being small in *M. crystallinum*, considerable in *M. tricolor*, and still greater in *Sedum*.

N. H. J. M.

Fermentative Fat-hydrolysis. EMIL HOYER (*Ber.*, 1904, 37, 1436—1447. Compare Abstr., 1903, i, 218).—The experiments were made with castor oil seeds as the source of the ferment. All attempts to obtain a solution of the ferment by extraction with various solvents or by Buchner's method were unsuccessful. The residue in the Buchner press possesses the full hydrolysing power of the unpressed seeds. In slightly germinated seeds, the half of the seed containing the shoot contains the smaller amount of ferment. As germination proceeds, the total amount of ferment in the seed diminishes.

A concentrated ferment may be obtained by repeated rubbing of the seeds with cotton oil and pressing through a cloth, the ferment being precipitated as a powder from the oil emulsion on addition of ether or carbon disulphide, or by washing the ground seeds by decantation with ether. These mechanical methods result in a concentration of the ferment, but are always accompanied by a loss owing to incomplete separation.

The hydrolytic effect of a given amount of ferment depends not on the water added, but on the amount of acid present. This amount differs for each acid. The limits within which the amount of any acid may vary are dependent on the nature of the acid; strongly dissociated acids must be present in exact proportion to the amount of ferment, slightly dissociated acids may vary considerably in amount. Carbon dioxide has no effect on the action of the ferment. G. Y.

Plant Constituents belonging to the Group of Non-nitrogenous Extract Substances. ERNST SCHULZE (*J. Landw.*, 1904, 52, 1—30).—Sucrose was found in seedlings, in the above-ground parts of young cereals and fodder plants, in leaves of trees, flowers, and in most seeds, yellow lupin seeds being the only ones in which it was not found. It was also obtained from the following plants before the flowering period: red clover, lucerne, vetches, rye, oats, Italian rye grass; a small amount was found in potato leaves.

Young rye and oat plants yielded scalose (Abstr., 1895, i, 165)

in addition to sucrose. A similar carbohydrate ($[\alpha]_D - 24.3^\circ$), possibly identical with secalose, was obtained from Italian rye grass. Other carbohydrates soluble in water occur, which yield mucic acid when oxidised.

As regards the substances (hemicelluloses) insoluble in water which are either not, or only very slowly, dissolved by diastatic enzymes, the author's results, obtained with a considerable number of plants, agree with those of Tollens in showing the frequency with which pentosans occur. In the majority of cases, galactose was obtained after hydrolysis.

In the case of seeds free from starch (lupins), the hemicelluloses serve as reserve cellulose, whilst in seeds containing starch (peas and vetches, &c.) they support the starch in its action during germination.

The cell-wall carbohydrates are, for ruminants, almost as important as starch, and more important than soluble carbohydrates such as sugar.

Some of the methods employed in separating and determining the different substances or groups are described. N. H. J. M.

Production of Asparagine. DMITRI N. PRIANISCHNIKOFF (*Chem. Centr.*, 1904, i, 1017; from *Ber. deut. bot. ges.*, 22, 35—43).—In accordance with E. Schulze's results, it was found that the concentration of asparagine in seedlings may exceed that in the cotyledons, or, in young seedlings, may be the same. It is not known whether the concentration of asparagine, like that of other amides, is higher in the cotyledons than in the axial organs.

Assuming that asparagine is produced chiefly or exclusively from the decomposition products of proteids, the two NH_2 groups must be derived from two molecules of one (or two different) primary amino acids, or else from diamino- or polyamino-compounds. The complete oxidation of the one amino-acid molecule would not be necessary as the primary decomposition products readily yield ammonia. In this manner, ammonium aspartate could be produced, and from this asparagine. The observations of Butkewitsch (*Tagsbl. XI. Naturforsch. Kongr.*, 1892, 387) (who found that, under the influence of anæsthetics, seedlings accumulate ammonia, whilst the formation of asparagine is retarded) lend support to this view. N. H. J. M.

Solution of the Nitrogenous Substances of Malt. L. PIERRE (*Chem. Centr.*, 1904, i, 1112; from *Mon. scient.*, [iv], 18, 190—193).—Potassium dihydrogen phosphate increased the solubility of the nitrogenous matter, especially at 60° ; the dipotassium salt had a similar effect, but in a less degree. With increased acidity, there was an increase of non-coagulable nitrogen at 15 — 68° , the effect being diminished in presence of calcium hydrogen carbonate. Precipitation of phosphoric acid at 15 — 68° was greatest, and the non-coagulable nitrogen was least, in presence of calcium hydrogen carbonate. Calcium sulphate increased the amount of non-coagulable nitrogen below 50° , and lowered the amount above 50° . Sodium chloride yielded the highest amount of non-coagulable nitrogen. N. H. J. M.

Composition of the Inner Fruit Shell of Coffee. BÉLA VON BITTÓ (*J. Landw.*, 1904, 52, 93—95).—The fresh substance had the following percentage composition :

| Water. | Ether extract. | Nitrogenous substance. | Non-nitrogenous extract. | Crude fibre. | Ash. |
|--------|----------------|------------------------|--------------------------|--------------|------|
| 11·18 | 1·15 | 5·50 | 20·66 | 58·87 | 2·63 |

The dry matter contains 0·58 per cent. of lecithin (calculated from the organic phosphorus), but no cholesterol, and 21·50 per cent. of pentosans.

The composition of the ash is as follows :

| K ₂ O. | Na ₂ O. | MgO. | CaO. | Fe ₂ O ₃ and Al ₂ O ₃ . | P ₂ O ₅ . | SO ₃ . | SiO ₂ . | Cl. | CO ₂ . |
|-------------------|--------------------|------|-------|---|---------------------------------|-------------------|--------------------|------|-------------------|
| 32·30 | 4·35 | 4·64 | 11·90 | 7·10 | 2·75 | 2·54 | 15·95 | 0·69 | 17·25 |

N. H. J. M.

Chemistry of Hips. KARL WITTMANN (*Zeit. landw. Versuchsves. Oesterr.*, 1904, 7, 68—74).—Analysis of four samples of the fresh fruit of *Rosa canina* gave the following results : water, 22·88—37·97 ; crude fibre, 19·86—25·24 ; nitrogen, 0·541—0·712 ; extract, 28·95—36·72 ; acids (as malic acid), 3·06—3·64 ; tannin, 2·00—2·69 ; total sugar (as invert sugar), 11·65—15·58 ; invert sugar, 10·20—13·76 ; sucrose, 0·59—2·43 ; crude fat, 1·72—2·59 ; and ash, 2·43—4·00 per cent.

The average percentage composition of the ash was as follows :

| K ₂ O. | Na ₂ O. | CaO. | MgO. | Fe ₂ O ₃ . | P ₂ O ₅ . | SO ₃ . | Cl. | SiO ₂ . | CO ₂ . |
|-------------------|--------------------|-------|------|----------------------------------|---------------------------------|-------------------|------|--------------------|-------------------|
| 23·53 | 2·40 | 26·78 | 7·73 | 0·52 | 9·37 | 3·65 | 0·30 | 0·67 | 25·38 |

The percentage of total ash is very high, and the calcium is higher than in any other fruit in the same zone. The amount of potassium is very low compared with other fruits.

N. H. J. M.

Migration and Return of the Nitrogen and the Chief Ash Constituents in the Leaf and Stem of Polygonum Sachalinense. JOSEF SEISSL (*Chem. Centr.*, 1904, i, 820 ; from *Zeit. landw. Versuchsves. Oesterr.*, 7, 39—58).—The plants were taken at intervals of 14 days from an area of 1·5 square metre, from June 15 to October 15. Potassium and phosphoric acid begin to return about the middle of June (when their amount is at its maximum), and continue until the end of the vegetative period. Calcium, magnesium, and sulphuric acid do not return, but go on accumulating. The loss of base due to the partial return of potassium is fully compensated by calcium.

The loss of potassium in the leaves and stems amounted to about one-half and two-thirds respectively, whilst the amount of calcium was doubled in the leaves and more than tripled in the stems.

N. H. J. M.

Rhubarb Cultivated in Berne (*Rheum Palmatum*, β -*Tanguticum*, and *Rheum Officinale* Baillon). P. A. A. F. EIJKEN (*Chem. Centr.*, 1904, i, 1077 ; from *Pharm. Weekblad.*, 41, 177—181).—Chrysophanic acid, emodin, isoemodin, C₁₅H₁₀O₅, rhein, C₁₅H₈O₆, and

anthraglucosides have been found in the rhizomes of *Rheum palmatum*, cultivated in Berne. The anthraglucosides, when hydrolysed by the action of dilute acids, yield chrysophanic acid, emodin, and rhein. The rhizomes of *Rheum officinale Baillon*, also grown in Berne, contained the same compounds with the exception of emodin, and the presence of chrysophanic acid, isoemodin, and rhein was detected in the roots. *Diacetylrhein*, $C_{15}H_6Ac_2O_6$, crystallises from glacial acetic acid in pale yellow needles and melts at 247—248°. E. W. W.

Seeds of Rhus Glabra. GEORGE B. FRANKFORTER and A. W. MARTIN (*Amer. J. Pharm.*, 1904, 76, 151—158).—The mature seed of *Rhus glabra* has been examined with the following results.

The whole seed yields 6·862 per cent. of moisture and 2·65 per cent. of ash; it consists of husk, 39·9 per cent., and kernel, 60·1 per cent. The ground seed, including the husk, was extracted successively with ether, alcohol, and water, and gave 22·36, 6·74, and 4·76 per cent. of extract respectively with these solvents.

The decorticated seed yields 4·93 per cent. of moisture and 1·98 per cent. of ash. On extraction with ether, it furnishes 9·1 per cent. of a pale yellow, mobile oil, which has a peculiar odour, a pleasant taste, becomes viscous at -18° , and solidifies at -24° . This oil has a sp. gr. 0·9203 at 20° and 0·9312 at 0° , and n_D 1·48821 at 0° and 1·48228 at 15° , is optically inactive, and is soluble in most organic solvents. Its absorption spectrum is peculiar, the violet rays being entirely absorbed and a black band appearing in the red portion. Rhus oil is a non-drying oil which gives a saponification value 194·7—195·3, and iodine value 85·96—87·86; on hydrolysis, it yields 8·35—9·28 per cent. of glycerol. It contains 0·696 per cent. of unsaponifiable matter, which consists of a cholesterol melting at 63·5—64°.

The husk of the seed contains 7·32 per cent. of tannic acid, 1·35 per cent. of calcium hydrogen malate, and 8·5 per cent. of a black, semi-solid, non-drying oil which has a sp. gr. 0·9412 at 20° and 0·933 at 35° . This oil gives an iodine value 87·2, and saponification value 179·7. When treated with acetone, about 80 per cent. of the oil dissolves and, on evaporating the solution, is obtained as a pale yellow liquid; the insoluble residue is a black, semi-solid substance.

E. G.

Assimilation of Iron by Spinach. O. VON CZADEK (*Chem. Centr.*, 1904, i, 832; from *Zeit. landw. Versuchswes. Oesterr.*, 7, 65—67).—By manuring the soil with 0·5 and 2 per cent. of ferric hydroxide, the percentage of iron in spinach plants grown in pots was increased from 0·03—0·18 and 0·23 per cent. on the dry matter. No effect on growth was observed at first, but later on the iron plants were somewhat retarded. N. H. J. M.

Influence of Betaine and of Amines on the Growth of the Sugar-Beet. KARL ANDRLÍK and VL. STANEK (*Zeit. Zuckerind. Böhm.*, 1904, 28, 291—297).—As it has been recommended to employ the residue from the desaccharification of molasses for the preparation of a nitrogenous and potash manure, the author has made experiments

to ascertain the influence exerted on sugar-beets by the application to the soil of betaine (which is the principal nitrogenous substance of these residues) and of the sulphates of dimethylamine and trimethylamine, these amines being formed in the decomposition of betaine. The results are briefly as follows: (1) in a soil rich in nitrogen, betaine acts favourably on the growth of the beet, but the purity of the juice is diminished (70·7 against 81·9), as also is the amount of sugar (10·2 against 13·25 per cent.); the amount of nitrogen in the roots is only slightly augmented. It is probable that the betaine does not pass as such into the roots, and, as it could not be detected in the soil at the end of the experiments, it presumably undergoes bacterial decomposition. (2) Small quantities of the amines used caused large increases in the root-growth, but the purity of the juice (70·9) and the amount of sugar (9 per cent.) were very low. The nitrogen present in the beets is also considerably augmented. In larger amounts, these amines produce a diminution in the root-growth. (3) Parallel experiments with ammonium sulphate led to much more favourable results than the preceding.

T. H. P.

Digestibility of Beet Sections Dried by Different Methods. OSCAR KELLNER, JAKOB VOLHARD, and FR. HONCAMP (*Bied. Centr.*, 1904, 33, 250—253; from *Deut. landw. Presse*, 1903, 30, 519).—The results of experiments in which sheep were fed with beet sections dried respectively in furnace gases and by a new process with steam showed that there was no considerable difference in the value of the two products.

N. H. J. M.

Nutritive Value of Whale Meal. ARNO KAOLI and SIGMUND HALS (*Bied. Centr.*, 1904, 33, 253—255; from *Norsk. Landmansbl.*, 1903, 22, 395—397).—A sample of fresh, lean whale flesh had the following percentage composition:

| Water. | Crude fat. | Crude protein. | Indigestible protein. | Digestible protein. | Ash. |
|--------|------------|----------------|-----------------------|---------------------|------|
| 81·58 | 0·86 | 17·34 | 0·30 | 17·04 | 0·39 |

The crude protein contained 14·5 per cent. of amides. The most striking results are the low ash, and the high digestibility of the proteids.

Analyses are also given of 27 samples of whale meal. These show a low digestibility, owing, no doubt, to the methods employed in their preparation.

N. H. J. M.

Fibre and Carbohydrates in Feeding-stuffs. Tentative Determination of the Components of Each. P. SCHWEITZER (*J. Amer. Chem. Soc.*, 1904, 26, 252—262).—The determinations were made by the official method and the chlorate and bromide methods in maize stems and leaves, timothy hay, red clover, and blue grass.

The true value for fibre is the crude fibre less the furfural-yielding constituents calculated as pentosan. To indicate its origin, the latter is given in the tables under the heading fibro-pentosan.

The substances left in the fibre by the bromine method and removed by treatment with acid and alkali are counted as pectoses. These also yield furfural. The results include, therefore, separate determinations of fibro- and pectose-pentosan in addition to the group of "pentosans" derived partly from sugar and starch, but chiefly from carbohydrates of unknown composition. N. H. J. M.

Influence of Artificial Manures on the Behaviour of Water in Soil. EMANUEL GROSS (*Bied. Centr.*, 1904, 33, 217—218; from *Zeit. land. Versuchswes. Oesterr.*, 1903, 80).—The rise of water in a tube containing fine soil alone was compared with that in similar tubes containing the same soil with 2 per-cent. of potassium sulphate, superphosphate, sodium nitrate, and calcium hydroxide respectively. It was found that lime retarded the upward rise of water.

Potassium salts and, in most cases, superphosphate, increased, whilst sodium nitrate and lime diminished the capillarity of the soil. In the case of lime, the diminution amounted to 30—40 per cent.

N. H. J. M.

Can Plant Analysis disclose the Amount of Assimilable Constituents in Soil? M. STAHL-SCHRÖDER (*J. Landw.*, 1904, 52, 31—92).—According to Heinrich (*Grundlagen zur Beurteilung der Ackerkrume, Wismar*, 1882), analysis of entire plants gives erroneous indications, and it is most convenient to confine attention to the roots (compare Dikow, *J. Landw.*, 1891).

The results of experiments with oats, made in 1893 and 1894, showed that with increased amounts of manure the corresponding constituents in the roots are also increased. The method can, however, give misleading results as regards the requirements of soils, although useful indications are obtained in extreme cases. It was found that other parts of the plants are affected by manuring as much as the roots, and can be employed with greater advantage, as the analysis of roots growing in soil is open to serious sources of error which are difficult to avoid.

As regards Atterberg's method, the author considers that his results do not show it to be impracticable, but that the influence of climate would have to be studied for several years, since some differences in composition were evidently due to the season.

N. H. J. M.

Action of Sterilised and Fermenting Organic Matter on the Solubility of the Phosphoric Acid of Tricalcium Phosphate. AXEL STÅLSTRÖM (*Centr. Bakt. Par.*, 1904, 11, 724—732).—The dissolving action of organic matter on tricalcium phosphate depends on the activity of micro-organisms. The nature of the fermentation is influenced by the character of the organic matter. In presence of peat, peat litter, manure, and broth, carbon dioxide-ammonia fermentation was observed; with milk, sour milk, and lactose, lactic fermentation, and with peat and lactose together butyric, fermentation.

Carbon dioxide-ammonia fermentation had very little action on tricalcium phosphate. With lactic and butyric fermentation, the effect was very distinct.

N. H. J. M.

Influence of Straw as Manure at Different Depths. CONRAD VON SEELHORST and W. FRECKMANN (*J. Landw.*, 1904, 52, 163—171).—Experiments with oats were made both with loamy and sandy soil in large pots, both with and without aëration, and with different amounts of water.

It was found that when the straw was mixed with the lower half of the soil there was a greater loss of nitrate and a greater injury to the plants than when mixed with the upper half when sodium nitrate had been applied, but in the case of the loamy soil (without nitrate) the presence of straw in the upper half was more injurious than when the straw was mixed with the lower half of the soil.

In the case of sandy soil, straw was more injurious in the subsoil than in the surface soil.

The injurious action of straw is attributed only to its being favourable to denitrification.
N. H. J. M.

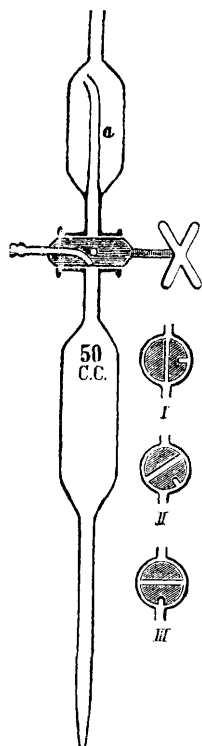
Influence of Straw Manure on the Yield in Presence of Lime or Sulphuric Acid. CONRAD VON SEELHORST and W. FRECKMANN (*J. Landw.*, 1904, 52, 172—174).—Both lime and sulphuric acid promote the decomposition of straw, and consequently diminish (without, however, entirely overcoming) the injurious effect of straw on crops.
N. H. J. M.

Analytical Chemistry.

Safety Pipette. WILHELM HIRSCHER (*Chem. Zeit.*, 1904, 28, 359).—A convenient automatic pipette, which will be readily understood from the accompanying figure.

The pipette is so fixed that the cross-handle of the stop-cock may be readily turned with the thumb. When in position I, the pump acts until the liquid appears in the overflow tube, *a*. The stop-cock is then at once turned through 45° into position II, which stops the further entrance of liquid. By further turning through 45° (III), the liquid runs out. By replacing the stop-cock in position I, the small quantity of liquid in *a* is forced into the overflow space. L. DE K.

Substitute for Burette Pinch Clamps. CARL KIPPENBERGER (*Zeit. anal. Chem.*, 1904, 43, 232—233).—In place of the short piece of glass rod slipped into the caoutchouc tube connecting the jet to the burette, which was suggested by Bunsen, the author prefers a short



piece of glass tube, open at its upper end, and having several holes pierced through its sides near the lower closed end. M. J. S.

Burette Stands. CARL KIPPENBERGER (*Zeit. anal. Chem.*, 1904, 43, 233—236).—The burettes are held in clamps so constructed that a number of them can be attached together in a row. Several forms of stand are figured, capable of carrying 9—12 burettes. M. J. S.

A Polarisation Colorimeter. AAGE A. MEISLING (*Zeit. anal. Chem.*, 1904, 43, 137—146).—This apparatus was designed for a hæmoglobinometer, but may be employed for general colorimetric estimations. The principle employed is that of producing by circular polarisation a coloured field which exactly matches the colour of the solution in a column the length of which can be measured. The instrument, which externally resembles a microscope, contains a pair of Nicol's prisms, with a quartz plate between them. The polarising prism and a reservoir for the coloured solution are placed close together on opposite sides of the axis of the tube. Into the solution dips a tube which is closed at the bottom by a thin glass plate and can be raised or lowered by a rack. The distance between this glass plate and the bottom of the reservoir gives the length of column of liquid, and can be read on a millimeter scale. A standard solution of the substance to be estimated is placed in the reservoir. The observer, looking through the upper Nicol, sees then two illuminated discs, and by rotating the analyser while varying the length of the coloured solution can obtain exactly the same colour in both discs. The analyser is then clamped. The standard solution is replaced by that which is to be estimated, and by varying the length of the column the same colour is reproduced. The percentage of the coloured substance is inversely proportional to the length of column required. A single cubic centimetre of solution, containing 5—20 cub. mm. of blood (diluted with a 0.1 per cent. solution of sodium carbonate), suffices for the observations, and it is shown that the length of column varies exactly with the dilution within wide limits. M. J. S.

New Indicator in Alkalimetry. LUCIEN ROBIN (*Ann. Chim. anal.*, 1904, 9, 130).—This indicator, which may be substituted for phenolphthalein, and has, moreover, the advantage of being applicable in the presence of ammonia, is prepared as follows: 10 grams of yellow mimosa flowers are mixed with 200 c.c. of water and heated to boiling; when cold, 50 c.c. of alcohol are added, and, after waiting for an hour, the liquid is filtered into a bottle made of brown glass. One drop of the indicator suffices for 10 c.c. of liquid to be titrated. On adding a drop of $N/10$ alkali, the liquid will turn golden-yellow and again become colourless on adding a drop of $N/10$ acid. Towards carbonates, it behaves exactly like phenolphthalein. L. DE K.

Detection of Chlorides in the Presence of Bromides. H. CHAPMAN JONES (*Chem. News*, 1904, 89, 229).—If silver chloride is treated with a cold saturated ammonium hydrogen carbonate solution for a few minutes and then filtered, the filtrate gives a distinct turbidity

when acidified with nitric acid. Silver bromide, when similarly treated, yields no turbidity. To ascertain whether a turbidity is due to silver chloride or bromide, the turbid solution is divided into two parts; to one is added a slight excess of the ammonium hydrogen carbonate solution, and to the other an equal quantity of water. If the turbidity is caused by silver chloride, it dissolves in a few seconds, but if due to the bromide it remains unaffected for nearly an hour. The part diluted with water serves as a comparison. W. P. S.

Detection of Free Chlorine and Bromine. DOMENICO GANASSINI (*Chem. Centr.*, 1904, i, 1172—1173; from *Boll. Chim. Farm.*, 43, 153—157).—A strip of filter paper immersed in a solution of 2 c.c. of aniline oil and 8 c.c. of hydrochloric acid in 40 c.c. of water turns wine-red when exposed to free chlorine and then becomes blue by exposure to the air. In the presence of bromides, the bromine should be first expelled by heating with potassium permanganate and acetic acid; the chlorine is then liberated by addition of a little sulphuric acid. In the presence of nitrous oxide, the paper turns yellowish-brown, changing in the air to greenish-blue. Paper is soaked in a saturated solution of potassium bromide, dried, and then immersed in an alcoholic ammoniacal solution of fluorescein. When dried and exposed to chlorine, it turns rose-red; bromine should be first expelled as directed.

As a delicate test for bromine vapour, the author recommends a paper which has been immersed in a 0.4 per cent. alcoholic solution of fluorescein containing a few drops of ammonia and then dried. A red colour shows the presence of bromine. Should chlorine be also present, the colour does not appear at first, but becomes visible when the paper is exposed to ammonia vapour. It is not discharged by exposure to acetic acid fumes. L. DE K.

New Reagents for Titration Purposes; Notes on Iodometry. FRITZ RASCHIG (*Zeit. angew. Chem.*, 1904, 17, 577—585).—A lengthy investigation unsuitable for useful abstraction.

A hydrochloric acid of absolutely known composition, and therefore fit for delicate standardising purposes, may be obtained by passing hydrogen chloride into a weighed amount of water and reweighing.

In a similar manner, a dilute solution of sulphur dioxide of known composition may be obtained and used for standardising iodine solution. The solution of sulphur dioxide should be added to the iodine solution, not the reverse. The reaction between dilute solutions takes place with such accuracy that the mixed hydriodic and sulphuric acids formed may be titrated with *N*/10 soda, using methyl-orange as indicator. L. DE K.

Estimation of Fluorine. E. DELADRIER (*Chem. Centr.*, 1904, ii, 1104—1105; from *Chem. Weekblad.*, 1904, i, 324—327).—Soluble fluorides are neutralised with ammonia and precipitated with lithium chloride, the precipitate being finally converted into sulphate. Or the

solution may be boiled with thorium chloride and the precipitate heated with ammonium nitrate, which converts it into thorium dioxide. Insoluble fluorides are mixed with 15 parts of powdered quartz and heated with sulphuric acid in a current of dry air at 160° . The gaseous compounds are first passed through a bulb containing precipitated silicic acid and then into a flask containing a layer of mercury and a sufficiency of water. After the heating has been continued for 3 hours, the separated silica is filtered off and the solution of hydrofluosilicic acid is precipitated with thorium chloride. After 24 hours, the thorium fluosilicate is collected on a weighed filter, dried, and weighed.

L. DE K.

Titration of Hydrofluoric Acid containing Hydrofluosilicic Acid. JULIUS KATZ (*Chem. Zeit.*, 1904, 28, 356—357, 387—389).—Ten grams of the previously diluted acid (1:10) are weighed in a platinum dish and titrated at the boiling heat with 2*N*-potassium hydroxide, using phenolphthalein as indicator; the result is expressed in terms of hydrogen fluoride. The operation may also be carried out in the cold in a paraffin-coated beaker, but then some calcium chloride should be added.

Ten grams of the same acid are now weighed out in a paraffin-coated beaker, diluted with 100 c.c. of 60 per cent. alcohol, and again titrated. The difference in c.c. between the two titrations represents the hydrofluosilicic acid. The factor to be used in the calculation varies, however, with the relation of the "difference" with the total number of c.c. used. If less than 5 per cent., 0.0576, if from 5—10 per cent., 0.0580—0.0595, if from 10—20 per cent., 0.060—0.061, and if over 20, 0.0617 is employed. The hydrofluosilicic acid thus found, multiplied by 0.833 gives the equivalent amount of hydrofluosilicic acid to be deducted from the result of the first titration. A full theoretical explanation is given.

L. DE K.

Estimation of Sulphur in Calcium Carbide. HJ. LIDHOLM (*Zeit. angew. Chem.*, 1904, 17, 558—560).—About 3 grams of the powdered sample are mixed with 15 grams of perfectly dry potassium sodium carbonate and 6 grams of perfectly dry ammonium chloride, and fused in a covered porcelain crucible, using a spirit burner as the source of heat. The fused mass is then introduced into a special apparatus, the air of which is displaced by a current of carbon dioxide, and then decomposed by means of hydrochloric acid. The gases evolved are passed through a series of absorbers filled with a solution prepared by dissolving 5 grams of cadmium acetate and 20 grams of zinc acetate in 200 c.c. of glacial acetic acid and diluting to 1 litre. The last traces of hydrogen sulphide are expelled by boiling while transmitting carbon dioxide.

The precipitate obtained is treated with 10 c.c. of a copper sulphate solution (120 grams copper sulphate, 120 c.c. sulphuric acid, water to 1 litre), which soon acts on the sulphides of cadmium and zinc, forming copper sulphide. This is then collected, washed, ignited, and weighed as oxide.

L. DE K.

The Sensitiveness of the Sodium Nitroprusside Reaction. C. REICHARD (*Zeit. anal. Chem.*, 1904, 43, 222—230).—A drop of a saturated solution of sodium nitroprusside gives an intense violet colour with 0.004 c.c. of an ammonium sulphide solution containing 0.0000018 gram of hydrogen sulphide. The sensitiveness of the reaction depends more on the concentration of the sulphide solution than on the absolute amount of sulphide. The same quantity of sulphur, whether in the form sodium sulphide or sodium or ammonium hydrosulphide gives the same intensity of reaction. Presence of excess of sodium hydroxide prevents the development of the violet colour; excess of ammonia has no such preventive action. The yellow solution obtained by saturating sodium hydroxide with sulphur does not give the violet colour with nitroprusside. The violet colour is in all cases ephemeral; its fading seems to be due to the oxidation of the sulphide to sulphite.
M. J. S.

Organically Combined Sulphurous Acid in Foods. K. FARNSTEINER (*Zeit. Nahr. Genussm.*, 1904, 7, 449—470).—The free and combined sulphurous acid (*Abstr.*, 1903, ii, 326) in solutions of sugars and other substances may be determined as follows: 20 c.c. of the solution, to which a little starch solution has been added, are titrated with iodine solution, to obtain the amount of free sulphurous acid. Five c.c. of 18 per cent. sodium hydroxide solution are then added, and, after 1 minute, 5 c.c. of hydrochloric acid of sp. gr. 1.124. The solution is then again titrated with iodine solution, when the quantity of combined sulphurous acid is obtained. Instead of hydrochloric acid, citric acid may be used. In the case of fruit juices, the most accurate results are obtained by distilling off the combined sulphurous acid after titrating the free portion. Numerous experiments are also described, in which the amount of sulphurous acid entering into combination with various sugars was ascertained.
W. P. S.

Estimation of Nitrogen. LÉON DÉBOURDEAUX (*Compt. rend.*, 1904, 138, 905—907).—The method consists in distilling the nitrogenous compound with a mixture of potassium sulphide and hyposulphite, whereby the nitrogen is converted into ammonia, and then weighed as ammonium chloride; it can be applied to the following types of compounds: (1) oxygenated compounds of nitrogen, (2) hydroxylamine, (3) nitrogen compounds containing a phenol grouping, (4) nitriles, cyanides, and double cyanides, (5) cyanates and thiocyanates, (6) unsubstituted amides and imides, (7) amines which contain an acidic grouping. Experiments in which the alkali sulphide was used by itself or with the addition of salts other than the hyposulphite were unsuccessful.
M. A. W.

Estimation of Nitrogen by Kjeldahl's Method. (*Trans. Guinness Res. Lab.*, 1903, 1, 13—16).—A distillation apparatus for use with Gunning's modification of Kjeldahl's method of estimating nitrogen in organic compounds is described, which is found to give good results. The vertical tube, through which the ammonia passes to the standard acid solution, is provided with a long, narrow condenser, and is furnished at its lower extremity with a bulb and wide tube leading into the receiving flask; the wide tube either

dips into the acid or drops the distillate on to its surface. The condenser is rendered necessary owing to the solvent action of the steam charged with ammonia on the glass, from which alkali is dissolved. Six of these distillation flasks, each of 1 litre capacity, may be arranged side by side, and their condensers connected up in series, the total space occupied being only about 90×25 cms.

When the estimation is made on natural products like barley, of which a large quantity must be taken for analysis, it is necessary to use a sufficient amount (20 or even 30 c.c.) of concentrated sulphuric acid to fully oxidise all carbonaceous matter and to leave an excess in which the potassium sulphate forms a tolerably liquid solution on cooling. Otherwise, if the flame under the flask is allowed to play on the unwetted surface of the glass beyond the limits of the acid mixture, as much as 90 per cent. of the nitrogen may be driven off by the superheating of the edges of the highly concentrated solution of sulphate.

T. H. P.

A Kjeldahl Apparatus. MAX SIEGFRIED (*Zeit. physiol. Chem.*, 1904, 41, 1—2).—To avoid spirting or “bumping” during the heating with sulphuric acid, the necks of the flasks are clamped to a bar, a slight swinging motion being communicated to the latter by means of a water or electric motor, so that the flasks move to and fro over the burners.

W. P. S.

Distilling Apparatus for Kjeldahl's Nitrogen Process. E. BLANCK (*Chem. Zeit.*, 1904, 28, 406).—The apparatus consists of a flask in which the substances are treated according to Kjeldahl's directions. It is fitted with a rubber stopper, bored to receive a tap funnel and also the connection to the distilling arrangement.

The funnel admits the alkali and the potassium sulphide; the distilling arrangement comprises the usual bulb, a condenser, and a pipette-shaped tube, the point of which dips into the standard acid contained in a receiver. Excepting the rubber cork, no other rubber connections are used. At the commencement, the water is allowed to run through the condenser at full speed, but towards the end it is made to run slowly, whilst the contents of the flask are being more vigorously boiled.

L. DE K.

Modification of Marsh's Apparatus. CASIMIR STRYZOWSKI (*Chem. Centr.*, 1904, i, 1228—1230; from *Österr. Chem. Zeit.*, 7, 77—81).—A modified form of the Marsh apparatus, which cannot be well understood without reference to the original paper and illustration.

The operation is conducted as usual after the air has been expelled by a current of carbon dioxide. As a sharp test for distinguishing a faint arsenical mirror from an antimonial one, it is recommended to heat the spot with a drop of dilute Fehling's solution, which is reduced by the arsenic but not by the antimony.

L. DE K.

Iodometric Estimation of Small Quantities of Arsenious Oxide. CARMELO RUSSO (*Gazzetta*, 1904, 34, i, 195—200).—For the detection of small quantities of arsenic, the author makes use

of Bloxam's method (Trans., 1860, 13, 12), in which, however, he employs sodium hydrogen sulphate or potassium hydrogen sulphate as electrolyte in place of sulphuric acid; the apparatus used by Bloxam is also modified so as to diminish the resistance. For quantitative estimation, an iodometric method is recommended, the hydrogen arsenide from the electrolytic apparatus being passed into a set of Geissler's bulbs containing a known volume of standard iodine solution, with which the following reactions take place: $\text{AsH}_3 + 3\text{I}_2 = 3\text{HI} + \text{AsI}_3$ and $\text{AsI}_3 + \text{AsH}_3 = 3\text{HI} + \text{As}_2$; the excess of iodine remaining in the bulbs is titrated with potassium arsenite in alkaline solution. For quantities of arsenious oxide up to about 0.01 gram, this method gives good results. The details are now being worked out.

T. H. P.

A New Indicator for Detecting Boric Acid, particularly in Food-stuffs. LUCIEN ROBIN (*Compt. rend.*, 1904, 138, 1046—1048. Compare this vol., ii, 440).—Tincture of mimosa gives a yellow colour with boric acid, becoming red on the addition of sodium carbonate. In order to detect traces of boric acid in the presence of other salts by means of this indicator, a strip of filter paper coloured with mimosa tincture is moistened with a concentrated acidified solution of the suspected mixture and then dried; if boric acid is present, the paper will be coloured yellow, and become a brick-red on the addition of sodium carbonate; in the absence of boric acid, the paper will be grey in colour, turning yellow on the addition of the alkali. To detect traces of boric acid in wines, ciders, &c., 10 c.c. of the liquid are neutralised with sodium carbonate, evaporated to dryness, and calcined, the residue is examined for boric acid as in the preceding case; by this means, the presence of 3 mg. of borax in 1 litre of wine can be detected. To detect boric acid in milk, the liquid is coagulated with acetic acid, filtered, and then treated in the same way as the wine.

M. A. W.

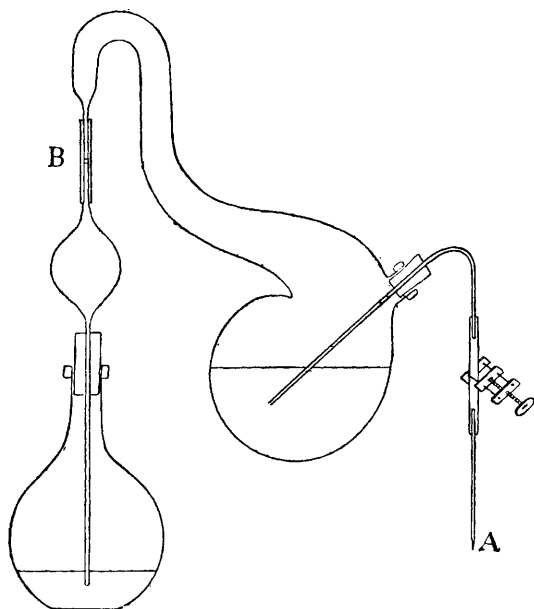
Estimation of Total Carbon in Coal and Soil. SAMUEL W. PARR (*J. Amer. Chem. Soc.*, 1904, 26, 294—297).—The substance is oxidised with sodium peroxide in the calorimetric bomb recently described by the author (Abstr., 1900, ii, 710), and, after decomposing the excess of the reagent by boiling with water, the carbon dioxide formed in the combustion is liberated and its volume measured, due allowance being, of course, made for any carbon dioxide contained in the sodium peroxide.

A convenient apparatus for measuring the carbon dioxide is described.

L. DE K.

Estimation of Carbon Dioxide in Alkalis and Alkali Carbonates. GIACOMO MARRO (*Atti R. Accad. Sci. Torino*, 1904, 39, 307—312).—The apparatus employed consists of a retort, the neck of which is bent. The retort, which has a capacity of 350—400 c.c., is one-third filled with distilled water to which a drop of phenolphthalein has been added; the water is boiled for two minutes to expel carbon dioxide, and a quantity of the dissolved alkali, containing about 0.2 gram of carbon dioxide, is then introduced by means of a pipette.

Fifty c.c. of standard baryta solution are measured into the flask and heated to boiling, whilst the liquid in the retort is simultaneously boiled for two or three minutes so as to completely expel the air from the retort and pipette; during this operation, the cork is not fixed in the neck of the flask, but at the end of it it is rapidly introduced and the burners taken away. Immediately afterwards, the point A is immersed in a mixture of sulphuric acid (1 : 1) with twice its volume of boiling water, so that the acid is sucked into the retort until the alkaline colour of the phenolphthalein is destroyed; the clamp on the india-rubber tube is then closed, the liquid in the retort gently boiled, a tube containing soda-lime is attached to A, and a slow current of air allowed to pass into the retort by carefully opening the screw-clip. The flame beneath the retort should be as small as possible. It is best



to surround the flask containing the baryta with warm water, and to then gradually cool this by adding cold water; in this manner, the liquid in the retort can be boiled for five minutes without a flame. After ten minutes' boiling, the flame is extinguished and a more rapid current of air admitted; the flask is detached, closed at B with a pinchcock, and shaken for 20 minutes to ensure complete absorption of the carbon dioxide. The residual baryta is then acidified with a slight excess of $N/5$ sulphuric acid, using phenolphthalein as indicator, and the excess of acid titrated by $N/20$ sodium carbonate. Very concordant results are obtained by using this method; the error due to the presence or absorption of atmospheric carbon dioxide is completely obviated.

W. A. D.

Analysis of Organic Substances with the Help of Sodium Peroxide. HANS H. PRINGSHEIM (*Amer. Chem. J.*, 1904, 31, 386—395. Compare this vol., ii, 146).—The method already proposed for the rapid estimation of chlorine, bromine, and iodine in organic compounds is described in detail. The reaction takes place more satisfactorily if, instead of sodium peroxide alone, a mixture of this compound with 4 per cent. of a carbohydrate is used.

In the case of liquid substances, a closed crucible is employed. The lid of this crucible can be screwed on, and is provided with a hole just large enough to hold a capillary glass tube into which is fused a copper wire connected to a piece of fine picture wire of such a length as to touch the bottom of the crucible. After the substance has been mixed with the sodium peroxide, the lid is screwed on and the crucible is connected to one pole of an electric battery, whilst the copper wire is attached to the other pole. The fine wire is thus fused and the mass inside the crucible is ignited.

The estimation of phosphorus and arsenic in organic substances can also be effected by means of sodium peroxide, but in these cases it is preferable to employ a silver crucible and to use a hot copper wire for starting the reaction in order to avoid the introduction of iron. In the case of phosphorus, the alkaline solution is acidified with hydrochloric acid and afterwards neutralised with ammonia and precipitated with magnesia mixture. In the case of arsenic, the alkaline solution is twice evaporated with nitric acid in order to oxidise the whole of the arsenious acid to arsenic acid, which is then precipitated according to the method of Friedheim and Michaelis (*Abstr.*, 1896, ii, 74).

An attempt was made to extend the use of sodium peroxide to the estimation of nitrogen, but so far the method has proved unsuccessful.
E. G.

Estimation of the Inorganic Constituents of Human Organs. MAX DENNSTEDT and THEODOR RUMPF (*Zeit. physiol. Chem.*, 1904, 41, 42—54).—To estimate the true mineral compounds in various organs such as the liver, &c., and also in blood, the finely divided organ should be treated with a large volume of water for 24 hours. The solution obtained is boiled to precipitate albumin, and, after the latter has been separated, is used for the different estimations. Sulphuric acid and phosphoric acid, present as sulphates and phosphates, are directly estimated as usual, whilst the calcium, magnesium, iron, &c., are estimated in the ignited residue from a known volume of the solution. An analysis of the ash of the organ does not show the real relation of acids to bases, as on ignition the organically combined sulphur and phosphorus form sulphates and phosphates with the bases.
W. P. S.

Estimation of Potassium in the Ash of Plants. EDWARD MURRAY EAST (*J. Amer. Chem. Soc.*, 1904, 26, 297—300).—The vegetable matter to be tested is drenched with a 20 per cent. solution of ammonium nitrate, dried, and incinerated at a moderate heat in a muffle. The ash so obtained is dissolved in the smallest possible quantity of hydrochloric acid, boiled, and mixed with a slight excess

of barium hydroxide. The filtrate is precipitated with a calculated amount of sodium sulphate and the filtrate concentrated to a small bulk. After acidifying with hydrochloric acid, the potassium is estimated by means of platinum chloride according to the conventional Lindo-Gladding method.

L. DE K.

Gasometric Estimation of Calcium, Barium, Strontium, Manganese, Potassium, and Copper. E. RIEGLER (*Zeit. anal. Chem.*, 1904, 43, 205—214).—The insolubility of the iodates of the above metals in dilute alcohol and their reaction with hydrazine sulphate allows them, when occurring singly, to be estimated by the same method as that adopted for ammonia (this vol., ii, 207). The general formula of the iodates of these metals is $M''(\text{IO}_3)_2$ (in the case of potassium, $\text{KH}_2(\text{IO}_3)_3$), and each IO_3 group yields in all cases 3N. The solution of the metal (10—15 c.c.) is mixed with excess (1 gram) of iodic acid, heated to ebullition, cooled, mixed with alcohol, shaken, and allowed to repose for 1—2 hours. The precipitate is then collected, washed with 95 per cent. alcohol until free from acid, and decomposed in the azotometer. If potassium has been precipitated as platinichloride, this may be dissolved in water and treated with iodic acid in the same way as any other potassium salt.

The copper salt, which, after drying over sulphuric acid at the ordinary temperature, has the composition $\text{Cu}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$, may be collected on a weighed filter and weighed.

M. J. S.

Reaction of Copper Salts [with Titanous Salts]. EDMUND KNECHT (*Mem. Manchester Phil. Soc.*, 1904, 48, [9], 1—4).—If titanous sulphate be added to a moderately concentrated solution of a cupric salt, immediate precipitation of metallic copper takes place. Owing to the difficulty of filtering the finely-divided copper, and to the fact that it rapidly oxidises and redissolves in the sulphuric acid present, the reaction cannot be used for the estimation of copper. With very dilute solutions of copper, the reaction requires from 2 to 30 minutes for its completion. A solution containing 0.001 per cent. of copper gives a distinct pink coloration when viewed by transmitted light. The reaction should be allowed to take place in the cold, as heating causes precipitation of titanous hydroxide.

W. P. S.

Estimation of Small Quantities of Mercury. THEODORE W. RICHARDS and SIDNEY KENT SINGER (*J. Amer. Chem. Soc.*, 1904, 26, 300—302).—The mercury is precipitated from its solution (as nitrate) by introducing a clean copper coil. When the bulk has apparently deposited, a second coil is introduced and left in the liquid for several hours. Free nitric acid should be practically absent. The amalgamated copper coils are washed with water, then with alcohol, dried in a desiccator over calcium chloride, and weighed. After heating at about 350° in a current of hydrogen, the coils are reweighed, and the loss represents the mercury.

L. DE K.

Estimation of Manganese by the Persulphate Method. HUGO LÜDERT (*Zeit. angew. Chem.*, 1904, 17, 422—423).—A slight

modification of the process introduced by von Knorre (*Abstr.*, 1903, ii, 760).

Four grams of the sample (free from tungsten) are put into a large flask and dissolved in 50 c.c. of boiling nitric acid of sp. gr. 1.2. The solution is diluted with 400 c.c. of water, 40 c.c. of sulphuric acid of sp. gr. 1.18, and 50 c.c. of ammonium persulphate solution (120 grams per litre) are added, and the whole is boiled for half an hour. The solution is rapidly cooled and mixed with 15 c.c. of hydrogen peroxide. This is made of such a strength that 10 c.c. correspond exactly with 9.4 c.c. of standard permanganate (1 c.c. = 0.00577 gram iron); the check should be made immediately before use. After the manganese peroxide has completely dissolved, the excess of hydrogen peroxide is titrated with the permanganate.

L. DE K.

Rivot's Estimation of Iron in the presence of Zirconium. ALEXANDER GUTBIER (*Zeit. anorg. Chem.*, 1904, 39, 257—258).—Polemical. A reply to Daniel (this vol., ii, 149).

A. McK.

Colorimetric Estimation of Iron in Blood by Meisling's Universal Colorimeter. H. P. T. OERUM (*Zeit. anal. Chem.*, 1904, 43, 147—159).—By converting the iron either into ferric thiocyanate (Jolles' method) or ferrocyanide, and the employment of Meisling's colorimeter (this vol., ii, 440), an estimation of the iron can be made with great accuracy in a quantity of blood not exceeding 0.1 c.c. The blood, measured with a fine pipette, is dried and incinerated in a porcelain crucible, the ash fused with 0.1 gram of potassium hydrogen sulphate, the fused mass dissolved either in 4 c.c. of 1 per cent. hydrochloric acid and treated with 1 c.c. of a 3 per cent. solution of potassium thiocyanate, or else in 3 c.c. of $\frac{1}{4}$ per cent. acid, and treated with 1 c.c. of a 0.5 per cent. solution of potassium ferrocyanide. The former solution must be examined immediately, as its depth of colour falls off in about 10 minutes, but it is easy to make 20 readings before this takes place. The latter mixture does not reach its maximum depth of colour for 2 minutes, but is then sufficiently stable to allow of 100 readings before the blue precipitate begins to separate in flocks. By taking the mean of 10 readings, the errors of individual readings are practically eliminated, and the results of different preparations agree closely.

M. J. S.

Separation of Iron and Chromium by means of Fused Potassium Nitrate. FRANK SOUTHERDEN (*Chem. News*, 1904, 89, 183).—The precipitate containing the hydroxides of iron, aluminium, and chromium is dried, placed in a test-tube, a little potassium nitrate is added, and the whole cautiously heated until fused. A small piece of potassium hydrogen sulphate is then added and the heating continued until brown fumes are evolved copiously. The chromium is thus completely oxidised and may be separated from the iron and aluminium in the usual manner. Even chrome-iron ore is decomposed sufficiently to give a decided reaction for chromium.

W. P. S.

Separation of Vanadium from Aluminium and Iron. B. GLASMANN (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 314—317).—To the solution containing vanadium together with aluminium or iron, sufficient potassium iodide and dilute sulphuric acid (1 : 5) are added and the mixture heated for 20 minutes, when the following reaction occurs: $V_2O_5 + 4HI = V_2O_3 + 2H_2O + 2I_2$; the iodine is dissolved by sulphurous acid. The solution is neutralised by the addition of potassium hydroxide until a precipitate begins to separate, this being then dissolved in a few drops of strongly diluted acid and the solution diluted to 100 c.c. with water. A few c.c. of a mixture of 20 per cent. potassium iodide and 7 per cent. potassium iodate solutions are then added, the aluminium or ferric sulphate acting thus: $Al_2(SO_4)_3 + 5KI + KIO_3 + 3H_2O = 2Al(OH)_3 + 3K_2SO_4 + 3I_2$; the precipitation of the ferric or aluminium hydroxide is completed by heating on the water-bath for half an hour. The iodine is dissolved in thio-sulphate and the ferric or aluminium hydroxide filtered off, washed well, ignited, and weighed. The filtrate containing vanadium trioxide is evaporated to dryness, with the addition, firstly, of sulphuric acid to remove the iodine, then of nitric acid to form vanadium pentoxide, and finally of sulphuric acid to displace the nitric acid. The residue is dissolved in water, acidified with sulphuric acid, mixed with sulphurous acid to reduce the V_2O_5 to V_2O_4 , and when the excess of sulphurous acid is removed by boiling and passing a stream of carbon dioxide through the liquid, the latter is titrated at 70° with potassium permanganate solution: $2KMnO_4 = 5V_2O_5$. The method is found to give good results.
T. H. P.

Cupellation of Platinum Alloys containing Silver or Gold and Silver. WILLIAM J. SHARWOOD (*J. Soc. Chem. Ind.*, 1904, 23, 412—413).—The experiments described were made to ascertain the extent to which lead is retained in the cupellation of platinum alloys, and also the extent to which the platinum dissolves during parting (this vol., ii, 151). The results show that the lead retained decreases, whilst the platinum dissolved by the nitric acid increases, with an increase in the ratio of silver to platinum. Silver and platinum remaining constant, an increase in gold appears to decrease the solubility of the platinum. The retention of lead seems to depend mainly on the fusibility of the button, oxidation ceasing for practical purposes when the button solidifies.
W. P. S.

Nicloux's Process for Estimating very Small Quantities of Alcohol. M. EMMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1904, 9, 126—129. Compare Abstr., 1902, ii, 233).—Nicloux has published a process for estimating very small quantities of alcohol, consisting in heating the distillate with sulphuric acid and standard solution of potassium dichromate until the latter is in slight excess, as shown by the greenish-yellow colour of the liquid. The author has again been unable to obtain concordant results, and is therefore unable to recommend the method.
L. DE K.

Estimation of Glycerol in Fats. RICHARD FANTO (*Zeit. angew. Chem.*, 1904, 17, 420—421).—The method is more particularly devised for the analysis of oxidised or partially saponified fats. Ten grams of the sample are saponified with 100 c.c. of $N/2$ alcoholic potassium hydroxide, 100 c.c. of water are added, the fatty acids are liberated by adding acetic acid, and the bulk of the alcohol is boiled off. When cold, the cake is detached and the liquid passed through a filter; the remaining glycerol may be obtained by melting the fatty acids about five times with about 20 c.c. of water. In the case of liquid acids, some paraffin wax may be added. The united aqueous liquids are now boiled down to 60—70 c.c., and when cold made up again to exactly 100 c.c. Five c.c. of this solution are then treated by the author's hydriodic acid process (*Abstr.*, 1903, ii, 515). L. DE K.

Action of Molybdates on Polyphenols and their Derivatives. C. FRABOT (*Ann. Chim. anal.*, 1904, 9, 123—124).—Ten grams of ammonium molybdate are dissolved in 100 c.c. of hot water, and when cold 10 c.c. of sulphuric acid are added. When a few drops of this reagent are added to a solution of quinol or *p*-phenylenediamine, or, in fact, to any para-derivative, a stable blue coloration is developed on boiling. L. DE K.

Dry Defecation in Optical Sugar Analysis. WM. D. HORNE (*J. Amer. Chem. Soc.*, 1904, 26, 186—192).—In determining the polarisation of a raw sugar, an error is introduced, owing to the fact that a precipitate is formed by the basic lead acetate added to the solution of the normal weight of sugar before making up to 100 c.c. In order to obviate this error, the author recommends defecating in such a way that the normal weight of sugar shall remain dissolved in 100 c.c. of the solution. This is done by making the solution of the normal weight up to 100 c.c., and then adding small quantities of powdered, anhydrous, basic lead acetate until the impurities are all precipitated. Some refinery solutions, notably such as have been subjected to the influence of bone-black, have a tendency to coat the grains of lead salt with insoluble adherent crusts, and so prevent the solution of the interior portions; this difficulty may be overcome by adding coarse, dry sand with the lead salt to the solution before shaking. Comparison of the numbers obtained by this method of working with those obtained by the old method, allowance being made for the volume occupied by the lead precipitate, shows that it gives good results.

T. H. P.

Rapid Estimation of Starch in Barley and Malt. (*Trans. Guinness Res. Lab.*, 1903, 1, 79—91).—For estimating starch in barley or malt the following rapid method has been devised; it is based on the cupric reduction only, and thus does away with the tedious extraction of the optically active amylans required by O'Sullivan's method (*Trans.*, 1884, 45, 1), as it has been found that these substances yield no reducing sugar when treated with malt diastase. The grain is first ground very finely in a Maercker mill, and about 5 grams of it are weighed out into a paper thimble, which is then

placed in an extraction apparatus. The flask of the latter is preferably round-bottomed and of copper, and to avoid over-heating the condensed vapours, the wide vapour tube of the extractor, which is essentially of the Soxhlet form, is connected with the top of one of the condenser tubes, of which two are rendered necessary by this arrangement; the wide vapour tube is also provided, near the lower end, with a bulb to prevent froth from passing into the condenser, and so into the extractor. Ether extraction is omitted, as the fats, besides not being a disturbing factor, are extracted equally well by the alcohol of sp. gr. 0.920, of which 80 c.c. are introduced into the copper flask, together with 0.5 gram of paraffin of high melting point to prevent frothing. The working of the apparatus is then adjusted so that the barley in the thimble is washed with alcohol of sp. gr. 0.900 for 3 hours (malt requires 9 hours), when the whole of the reducing substances and the nitrogen compounds soluble in alcohol are removed. No starch passes over into the extract. The contents of the thimble are now transferred to a beaker containing about 100 c.c. of water, and the whole thoroughly boiled. After cooling to 57°, 10 c.c. of an active malt-extract are added, and the conversion allowed to proceed for 60 minutes. The solution is then boiled, filtered into a 200 c.c. flask, the residue well washed, and the volume adjusted after cooling. The cupric reduction of 20 c.c. is next determined under the standard conditions laid down by Brown, Morris, and Millar (*Trans.*, 1897, 71, 94), and the maltose calculated from the copper reduced according to Table XI (*loc. cit.*, p. 100), after allowing for the reduction due to the malt-extract. The starch equivalent of this maltose is then ascertained, assuming, if the conditions of the theoretical conversion of starch into maltose and dextrin ($10C_{12}H_{12}O_{10} + 8H_2O = 8C_{12}H_{22}O_{11} + 2C_{12}H_{20}O_{10}$) have been complied with, that 84.4 parts of maltose correspond with 100 of starch. To bring the conversion down to this point, malt dried on the kiln at 50–52° and having a diastatic power of 80 on Lintner's scale must be employed. If a less diastatic malt is used, the amount of maltose formed per 100 of starch must be determined by a preliminary experiment with pure starch; [malt having a diastatic power of 40 Lintner yields only 82 parts of maltose per 100 of starch. Malts with higher diastatic powers than 80 carry the conversion beyond the stage represented by the above equation.

A determination of the moisture in the barley or malt is carried out at the same time as the estimation of the starch, which is then calculated on the dry matter of the barley or malt. T. H. P.

Lintner's Soluble Starch and the Estimation of "Diastatic Power." JOHN S. FORD (*J. Soc. Chem. Ind.*, 1904, 23, 414–422).—Attention is drawn to the necessity of observing certain precautions in this estimation, and the author considers that many of the contradictory results obtained by various observers are due to the lack of recognition of the important influence of traces of impurity on the course of the action. The latter attains its maximum in neutral solution. Asparagine does not augment the action unless there has been a previous restriction. This also applies to the various salts which are said to accelerate the action. The restricting influence of

acids depends on their dissociation—the greater the amount of free hydrogen ions, the greater the restriction, although it is possible that the anion of certain acids may have some influence. Properly purified soluble starch, or starches, of various origins give equal maltose productions, with equal amounts of diastase, under standard conditions. An example is given of the “diastatic power” of a malt as estimated with different soluble starches bought from dealers. The results obtained varied from 34 to 6 on Lintner’s scale. W. P. S.

Estimation of the Mono-amino-Acids and their Amides. (*Trans. Guinness Res. Lab.*, 1903, 1, 17—56).—A critical examination of the methods previously given for the estimation of amides and amino-acids, together with an account of improvements in these methods and of new methods which have been devised.

The first process examined was that which Sachsse (Abstr., 1873, 652) gave for the estimation of asparagine, which is based on its hydrolysis into aspartic acid and ammonia when boiled with 10 per cent. hydrochloric acid. On determining the ammonia formed by Knop’s hypobromite method, results considerably in excess of the proper values were obtained. Replacement of the hydrochloric acid by 5 per cent. oxalic acid solution gave much better results, which were, however, not obtainable in all cases. On estimating the ammonia formed by hydrolysing asparagine by hydrochloric acid (10 c.c. concentrated acid diluted to 100 c.c.) by distillation with magnesia at 35° under reduced pressure in a specially designed apparatus, the numbers obtained were constantly 5 per cent. below the theoretical ones, so that the authors propose to employ this method and to increase the values arrived at in the proportion of 95:100. Using 5 per cent. oxalic acid solution as the hydrolysing agent, equally concordant results were obtained, but in this case a 10 per cent. correction must be applied; the hydrolysis is, in this case, much slower than when hydrochloric acid is used. It is concluded that the reaction involved in the hydrolysis of asparagine by oxalic or hydrochloric acid cannot be truly represented by the usually accepted equation in which one mol. of asparagine yields one mol. of ammonia, and that the apparently theoretical results obtainable with the hypobromite method under certain conditions are due to some secondary reaction tending to augment the volume of nitrogen obtained.

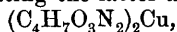
Next is given a description of an apparatus for determining amino-acids and their amides by a modification of Sachsse and Kormann’s method (Abstr., 1875, 784), which is based on the reaction of these substances with nitrous acid, by which means they give up the whole of their nitrogen in the gaseous state. The air in the apparatus is displaced by pure carbon dioxide, and the ferrous sulphate originally employed for absorbing the nitric oxide formed is replaced by oxygen, the excess of which is subsequently absorbed by alkaline pyrogallol solution. Under these conditions, good results are obtained with asparagine, aspartic acid, glutamic acid, leucine, alanine, glycine, and phenylalanine. Tyrosine gives unsatisfactory results with nitrous acid, but after previous bromination normal values are obtained; the brominated solution must, however, only be introduced into the

apparatus after expulsion of the air, otherwise low numbers are always arrived at.

Tyrosine may also be estimated as *dibromotyrosine*, $C_9H_9O_3NBr_2$, which may be prepared by treating a dilute hydrochloric acid solution of tyrosine with an excess of potassium bromide and the calculated quantity of sodium bromate; it crystallises from water in well-formed, flat prisms melting at 222° , has a feebly acid reaction to litmus, and does not form a salt with hydrochloric acid, but yields an extremely insoluble *copper* compound, $(C_9H_8O_3NBr_2)_2Cu$, which may be used to separate it from a mixture. The estimation of the tyrosine is carried out as follows: a weighed quantity is dissolved in 20 per cent. hydrogen chloride solution, which is mixed with 10—15 c.c. of a 20 per cent. potassium bromide solution, and then titrated with *N*/5 sodium bromate solution; the end of the reaction is easy to observe, the last drop of bromate solution required giving a persistent, deep yellow colour, but if the original solution is coloured, starch and potassium iodide may be used as an indicator.

The following scheme for estimating ammonia, amidic nitrogen, and amino-acid nitrogen gives good results: (1) the total nitrogen is determined by Kjeldahl's method. (2) The ammonia present is determined by distillation in a vacuum at 35° with magnesia (*vide supra*). (3) A measured portion of the solution is hydrolysed with 10 per cent. hydrochloric acid for 2 hours, thus liberating one-half of the nitrogen of the amide as ammonia. The ammonia is then estimated by distillation with magnesia in a vacuum, a correction of 5 per cent. being added for the constant error. From the ammonia thus found is deducted that originally present as such [see (2)], the remainder being a measure of the nitrogen present as amidic nitrogen. (4) A portion of the original solution is then submitted to the modified Sachsse-Kormann process described above, any tyrosine present being previously brominated. The nitrogen thus obtained, diminished by the amide nitrogen found by (3) and then divided by two, gives that present in the form of amino-acids. (5) Tyrosine, if present, is determined directly by the bromine method, and on deducting its nitrogen equivalent from the total nitrogen of the amino-acids determined in (4), the nitrogen of the amino-acids other than tyrosine is arrived at.

Following the suggestion of Schulze (Abstr., 1883, 315), it is found that mercuric nitrate may be employed as a precipitant for asparagine. Excess of this reagent is added, in the cold, to the asparagine solution, and the precipitate filtered off and washed with water. The acid filtrate is then rendered slightly alkaline by means of sodium hydroxide solution and the precipitate thus obtained added to the first one, the whole being then treated with hydrogen sulphide to liberate the asparagine. On separating the latter as its copper salt,



by the addition of copper acetate to a solution rendered slightly acid with acetic acid, which is afterwards removed by evaporation, it is found that the whole of the asparagine is recovered. With aspartic acid, this method only allows of the recovery of 89.3 per cent. of the original quantity of acid.

T. H. P.

Estimation in Barley and Malt of the Total Amount of Nitrogenous Substances Soluble in Water. (*Trans. Guinness Res. Lab.*, 1903, 1, 61—78).—The conditions have been investigated under which the soluble nitrogenous constituents of barley and malt may be extracted in order to show the changes occurring in these substances during germination. To avoid the difficulties introduced by the diminution in weight of the grain during malting, all the determinations are calculated with reference to the weight of dry matter in 1000 corns of the original barley. In making the extractions, it is found that the time of digestion and the ratio of grain to water influences the results considerably, due, in the former case, to proteolytic changes taking place, and in the latter to changes of solubility of proteids such as the globulins, produced by changes in the concentration of the mineral salts present. The standard conditions chosen to overcome the latter difficulty were such that, whether dealing with barley or malt, the total final volume of extract and residue together always contained the equivalent of 20 grams of the original dry barley per 100 c.c.; the volume of the mixture during the extraction was taken as three-fourths of the final volume, which was made up subsequently.

The finely-ground sample was mixed in a flask with the required amount of water, and the stoppered flask fixed radially on a rotating wheel and shaken for 6 hours, after which the volume was made up and the whole filtered. The nitrogen was then determined in the filtrate, both directly and after boiling, to remove coagulable substances; the volume of the dried residue was then calculated from its weight and specific gravity and the results expressed with reference to the original dry barley.

Extraction with 5 per cent. sodium chloride solution instead of water caused a marked increase in the nitrogenous matter extracted. The addition of salicylic acid to the water exerted no restricting action on proteolysis during prolonged extractions.

The following table gives the results obtained, under the above conditions, with a mellow, thin-skinned Wiltshire barley and the malt prepared from it.

| Solvent. | Percentage of nitrogen extracted in six hours from dry barley or its malt equivalent. | | | Percentage of nitrogen calculated on amount present in 20 grams of original barley (dry). | | |
|------------------|---|--------------|------------------|---|--------------|------------------|
| | Total. | Co-agulable. | Non-co-agulable. | Total. | Co-agulable. | Non-co-agulable. |
| <i>Barley :</i> | | | | | | |
| Water | 0.251 | 0.090 | 0.161 | 14.7 | 5.3 | 9.4 |
| 5% NaCl solution | 0.388 | 0.128 | 0.260 | 22.8 | 7.5 | 15.2 |
| <i>Malt :</i> | | | | | | |
| Water | 0.523 | 0.142 | 0.381 | 30.7 | 8.3 | 22.4 |
| 5% NaCl solution | 0.669 | 0.212 | 0.457 | 39.3 | 12.5 | 26.8 |

With air-dried malt, it is possible that a certain amount of proteolytic action occurs during the standard 6 hours' extraction.

T. H. P.

Iodine Value of Unsaturated Organic Compounds.

HARRY INGLE (*J. Soc. Chem. Ind.*, 1904, 23, 422—428).—The results of the work described confirm the conclusions arrived at in a previous paper (Abstr., 1902, i, 528), and also show that the amount of acid formed probably depends on the ionisation and subsequent hydrolysis of the iodochlorides by the water present. The amount of this hydrolysis is dependent on the nature of the groups attached to the double linking. The presence of aromatic groups and of negative groups in an unsaturated compound attached to the ethylene linking tend to lessen its attraction for iodine chloride in proportion to their negative character. The iodochlorides are further proved to be reduced by the action of aqueous potassium iodide, and this reduction is considered to be a fertile source of error in the estimation of the iodine values of unsaturated compounds. By estimating the iodine value of a substance by the various solutions (Hübl, Wijs, &c.) and the amount and nature of the acid produced by the hydrolysis, some information may be obtained as to the position of the ethylene linkings in the molecule. The triply-linked carbon pairs seem to exert less attraction for iodine chloride than the doubly-linked.

W. P. S.

Iodine Absorption of Oil of Turpentine. THOMAS F. HARVEY (*J. Soc. Chem. Ind.*, 1904, 23, 413—414).—The author finds that the quantity of halogen absorbed by oil of turpentine from Wijs's solution is governed by the excess of solution used and also by the character of the excess halogen present in the Wijs solution, that is, whether iodine or chlorine is present in addition to iodine monochloride. The time of contact has also some slight effect on the amount absorbed. Solutions containing an excess of chlorine gave considerably higher values than others in which iodine was in excess.

W. P. S.

Characteristics of some Almond and Allied Oils. JULIUS LEWKOWITSCH (*Analyst*, 1904, 29, 105—110).—The results of analyses of several samples of almond oils, apricot kernel oils, and peach kernel oils of undoubted genuineness are given. From the figures obtained, it is seen that these oils cannot be distinguished from each other by means of their chemical and physical constants. As regards the colour reactions, Bieber's test was the only one that gave any indications. This test consists in treating 5 parts of the oil with 1 part of an equal mixture (by weight) of sulphuric acid, fuming nitric acid, and water. Pure almond oil does not change colour, whilst peach kernel oil assumes a peach-blossom tint. The phloroglucinol test (Abstr., 1903, ii, 114) was found to be untrustworthy.

W. P. S.

Tunisian Olive Oil. E. MILLIAU (*Chem. Centr.*, 1904, i, 1026—1027; from *Bull. Direction Agric. et Comm. Tunis*, 1903, 493).—Bellier and Kreis's colour reactions with a solution of resorcinol in

benzene or of phloroglucinol in ether are to be preferred in the case of Tunisian olive oil to Becchi and Baudouin's tests, which give a yellow coloration with the unadulterated oil. The presence of earth nut oil is detected by Bellier's method. A mixture of adulterated or of pure Tunisian oil with an equal volume of glacial acetic acid at 100° forms a clear solution, but if colza oil is present the solution on cooling becomes turbid, whilst the pure oil under similar conditions remains clear even at much lower temperatures. The iodine number is determined by Bellier's method, of which details are given in the original. The results obtained by this method are more accurate in the case of solid fats than of oils, the values found in the latter case being generally too high. A method of estimating the iodine number by measuring the rise of temperature with a mixture of 1 gram of oil and 10 c.c. of chloroform or acetic acid is also described in the original paper. The presence of hydrocarbons is detected by determining the portion which is not hydrolysed by a concentrated solution of potassium hydroxide. Oils from Sfax and Tunis have been saponified and the fatty acids converted into dihydroxystearic acid by the action of potassium permanganate. In order to determine the acetyl number, the fatty acids were boiled with acetic anhydride, the product hydrolysed by potassium hydroxide, and the acetic acid, obtained by adding sulphuric acid and distilling in steam, was estimated by titration. By this method, the simultaneous formation of fatty anhydrides is avoided. Sfax olive oil has an acetyl number 262, the Tunis oil 203, and pure ricinus oil 153.

E. W. W.

Quantitative Separation of the Pyridine Bases from Ammonia and the Aliphatic Amines. JAR. MILBAUER and VL. STANĚK (*Zeit. anal. Chem.*, 1904, 43, 215—222).—Ammonia and the aliphatic amines combine directly with carbon dioxide, but the pyridine bases do not. If, therefore, a mixture of these is treated with carbon dioxide and calcium chloride, or their salts with calcium hydroxide, the ammonia and amines are converted into chlorides (by reaction of their carbonates with the calcium salt), whilst the pyridine bases remain free and can be extracted with ether. The extraction is, however, tedious. A more rapid and equally efficacious method depends on the insolubility of ammonium carbonate in ether. The solution containing ammonia, aliphatic amines, and pyridine is accurately neutralised, saturated with sodium chloride, mixed with an excess of saturated sodium hydrogen carbonate solution, and shaken twice for 15 minutes with an equal volume of ether.

The pyridine in the ethereal solution can then be accurately titrated by $N/10$ sulphuric acid, using as indicator Patent Blue VN superfine. This indicator is green in presence of the excess of acid added, but turns blue sharply when the excess is exactly neutralised by $N/10$ alkali.

M. J. S.

Arsenical Sulphuric Acid as an Alkaloidal Reagent. LEOPOLD ROSENTHALER and F. TÜRK (*Chem. Centr.*, 1904, i, 1106; from *Apoth. Zeit.*, 19, 186—187).—A solution of 1 gram of potassium arsenate in 100 c.c. of sulphuric acid is stated by the authors to be a special

reagent for the identification of opium alkaloids. It must, however, be remembered that hydrastine and hydrastinine behave somewhat like narcotine. Cryptopine, papaverine, and thebaine also give the same reactions with pure sulphuric acid alone. If 0.1 mg. of the alkaloid is mixed with 0.1 gram of oxalic acid and then gently heated with 1 gram of the reagent, the following effects are noticed: morphine, grass-green to bluish-green; apomorphine yellowish-green to grass-green; dionine, grass-green, heroine, grass-green to bluish-green; narcotine, purple to carmine; codiine, blue to violet. For further particulars, the original paper should be consulted.

L. DE K.

The André [Thalleoquinine] Reaction for Quinine. EUGÈNE LÉGER (*J. Pharm. Chim.*, 1904, [vi], 19, 281—284).—Small quantities of quinine may, as is well known, be detected by the green colour produced on adding chlorine or bromine water, and then ammonia.

It appears from the author's experiments that if bromine water is employed this should be added very cautiously, as an excess will prevent the reaction altogether. Used with care it is, however, a very delicate test.

L. DE K.

Evaluation of Quinine by André's Reaction. EUGÈNE LÉGER (*J. Pharm. Chim.*, [vi], 19, 434—435).—A criticism of the process for testing cinchona bark described in both the Swiss and Italian pharmacopœias. The depth of coloration caused by the action of bromine water and ammonia is a quite untrustworthy guide for judging the amount of quinine.

L. DE K.

Estimation of Quinine in the presence of Other Cinchona Alkaloids. EUGÈNE LÉGER (*J. Pharm. Chim.*, [vi], 19, 427—434. Compare Abstr., 1902, i, 549).—Quinine cannot be quantitatively separated from cinchonidine by ether. Crystallisation as sulphate only succeeds when the quinine strongly predominates, and Oudemans's polarisation process may fail in practice on account of the co-precipitation of other tartrates besides quinine and cinchonidine.

The object may, however, be successfully attained by first purifying the sulphates by recrystallisation from boiling water (previously saturated in the cold with quinine sulphate). A portion of the product so obtained is dissolved in boiling water, previously saturated in the cold with both quinine and cinchonidine tartrates. A calculated amount of potassium sodium tartrate is added, and, after 24 hours, the mixed tartrates of quinine and cinchonidine are collected on a tared filter, washed with a cold-saturated quinine tartrate solution, then with a very little water, air-dried, and weighed. The quinine tartrate contained therein may now be accurately determined by observing its rotatory power α_m , and applying Oudemans's formula, $215.8 \times 2 + 131.3(100 - \alpha) = 100 \times dm$.

L. DE K.

Xanthine Bases contained in Meat, Yeast, and other Extracts.
II. **The Xanthine Bases of Yeast Extract.** KARL MICKO (*Zeit. Nahr. Genussm.*, 1904, 7, 257—270).—A somewhat similar method to

that described under meat extract was employed (Abstr., 1902, ii, 369; 1903, ii, 101). Three hundred grams of yeast were boiled with 2300 c.c. of water and 200 c.c. of dilute sulphuric acid (1:3). The hydrochloric acid solution of the bases obtained from the copper hydrogen sulphite precipitate was evaporated and treated with ammonia for 12 hours. The precipitate formed (Fraction I) was separated and washed. After precipitating the filtrate with silver solution and removing the silver from the precipitate, the hydrochloric acid solution of the bases in the latter was evaporated and the residue obtained treated with boiling picric acid solution. The precipitate (Fraction II) was collected in a filter, and evaporation of the filtrate yielded further amounts of bases (Fractions III and IV). These fractions were purified and refractionated. Fraction I consisted principally of guanine, traces of adenine, xanthine, and hypoxanthine also being present. Adenine was the only base detected in Fraction II. In comparison with the other fractions, Fraction III contained the largest quantity of xanthine. Besides the latter, hypoxanthine was present, together with small amounts of guanine and adenine. Fraction IV consisted mainly of hypoxanthine, mixed with traces of xanthine, adenine, and guanine. Adenine is the chief constituent of the xanthine bases found in yeast extract, then follow guanine, hypoxanthine, and xanthine. Carnine was not detected. W. P. S.

Decomposition of Tannin Solutions. EDOUARD NIHOUL and L. VAN DE PUTTE (*Chem. Centr.*, 1904, 1, 840—841; from *Bull. Assoc. Belge des Chimistes*, 17, 390—398).—Experiments showing that infusions of oak bark, pine bark, and sumach rapidly deteriorate, which may cause discrepancies in analysis. In the case of oak bark, the decomposition may be retarded by addition of a little thymol.

L. DE K.

Behaviour of Certain Organic Compounds towards Blood, especially as regards the Detection of Blood. OSKAR ADLER and RUDOLF ADLER (*Zeit. physiol. Chem.*, 1904, 41, 59—67).—Tabulated results are given of a number of experiments, in which the colour reactions of various aromatic amines, and acids, and of phenols of the diphenyl and naphthalene series, with blood in the presence of hydrogen peroxide are compared. It was found that the higher members of the series exhibited the greater sensibility. Catechuic acid and benzidine would detect 1 part of blood in 100,000 parts of water, or 0.001 per cent.

A solution of pure leuco-base of malachite-green (tetramethyldiaminotriphenylmethane) in glacial acetic acid is also an extremely sensitive reagent, giving an intense green coloration with solutions containing 0.001 per cent. of blood, after the addition of a little hydrogen peroxide. In preparing the reagent, it is advisable to shake the acetic acid solution with an equal volume of chloroform, and then to add water cautiously until the latter separates. Any green coloration which the original solution may have is thus removed. In testing urine for blood, about 15 c.c. of the urine are extracted with ether, the ethereal layer is drawn off, and then treated with hydrogen

peroxide and the reagent. In the case of fæces, a little of the latter is mixed with water and the unfiltered solution tested with an alcoholic solution of benzidine in the presence of hydrogen peroxide and a drop of acetic acid, an intense green colour being produced should blood be present.
W. P. S.

Detection of Urobilin in Urine. LÉON GRIMBERT (*J. Pharm. Chim.*, [vi], 19, 425—426).—Thirty c.c. of urine are mixed with 20 c.c. of Dénigé's reagent, and after 5 minutes the filtrate is agitated in a separating funnel with 5 c.c. of chloroform. The chloroform is introduced into a test-tube, and Roman and Delluc's reagent is added as long as it produces a turbidity (10 drops are usually required). The moment the liquid becomes clear, the characteristic green fluorescence will be noticed.

Preparation of the reagents.—Dénigé's solution is prepared by dissolving 5 grams of yellow oxide of mercury in 100 c.c. of water and 20 c.c. of pure sulphuric acid. Roman and Delluc's solution is made by dissolving 10 grams of zinc acetate in 100 c.c. of 95 per cent. alcohol and a few drops of acetic acid.
L. DE K.

Estimation of Bile Salts. OTTO GRÜNBAUM (*Trans. Pathol. Soc. Sweden*, 1904, 55, 55—59).—A full account of the method previously described (this vol., ii, 103).
W. D. H.

Estimation of the Proteolytic Capacity of Malt. PHILIP SCHIDROWITZ (*J. Inst. Brewing*, 1904, 10, 166—172).—In order to obtain concordant results in this estimation (Abstr., 1903, ii, 680), particular attention should be paid to the quality of the gelatin used. The latter should be neutral or slightly acid to litmus. Alkaline gelatins must be rejected. To prepare a standard gelatin solution, about 3 grams of the sample are dissolved in 200 c.c. of water and titrated with *N*/10 sodium hydroxide solution, using phenolphthalein as indicator. Sixty-four grams of the gelatin are then dissolved in 500 c.c. of hot water (measured at 15°), an amount of *N*/10 sodium hydroxide solution, as determined in the preliminary titration, is added, and the whole diluted to 736 c.c. After cooling to about 45°, the white of an egg is added, the mixture is heated to 90° on a water-bath, filtered through paper, and cooled to 60°, when 4 grams of powdered thymol are added. The jelly is kept in well-stoppered bottles. The quantities of water mentioned above refer to gelatins containing 16.8 per cent. of water.
W. P. S.

General and Physical Chemistry.

Spark Spectrum of Radium. CARL RUNGE and J. PRECHT (*Ann. Physik*, 1904, [iv], 14, 418—422. Compare Abstr., 1903, ii, 346, 621).—The authors have used a purer specimen of radium bromide than was available in their earlier work, and have observed a number of new lines, especially in the red part of the spectrum. J. C. P.

Penetrating Rays of Radium. FRIEDRICH PASCHEN (*Ann. Physik*, 1904, [iv], 14, 164—171).—It is shown that the γ -rays from radium are like the β -rays in that they carry negative electricity with them. The former, however, are absorbed to a much smaller extent, and so the velocity of the γ -radiation is probably greater than that of the β -radiation. The highest velocity hitherto deduced for the latter has been about 1/18th that of light, and it is therefore possible that the case of electricity moving with the velocity of light may be realised in the γ -rays. J. C. P.

Cathode Rays of Radium. FRIEDRICH PASCHEN (*Ann. Physik*, 1904, [iv], 14, 389—405).—A quantitative study of the behaviour of the γ -rays in a magnetic field bears out the view recently adopted (preceding abstract) that these are cathode rays of very high velocity. J. C. P.

Radioactive Substances in Relation to the Presence of Helium. RAFFAELLO NASINI (*Atti R. Accad. Lincei*, 1904, 13, i, 367—368).—Barium sulphate prepared from the Abano deposits has at first but slight radioactivity, which, however, increases very considerably after a time. The same is the case with the chloride prepared from the sulphate. By treating this chloride, after it has reached its maximum activity, with sodium amalgam and preparing the active chloride from the amalgam thus obtained, an increase is obtained in the activity, which, by repetition of this process, may attain a value seven times as great as that of the original chloride. Other products, such as the incrustations, from the Abano springs are, under these same conditions, either more or less active than the deposits, but are less convenient to concentrate than the latter.

Both the gas from the soffioni, and the emanations from the rocks, at Larderello are appreciably radioactive and the activity diminishes as time goes on, but the diminution does not appear to proceed in agreement with that observed for radium emanations. T. H. P.

Radioactivity of the Gases evolved from the Waters of Thermal Springs. PIERRE CURIE and A. LABORDE. (*Compt. rend.*, 1904, p. 1150—1153).—Each gas was enclosed in a cylindrical brass condenser and the saturation current measured in the usual manner. In every case it was observed that the current increases rapidly for

some hours after the introduction of the gas; a maximum value is reached, after which the current strength gradually falls until, in about twenty-four hours, the rate of decay is the same as that shown by radium emanation. A list of the gases examined is given, together with the value in electrostatic units of the current four days after the gas had been collected from the spring, whilst a second column shows the number of minutes during which 1 mg. of radium bromide must be allowed to remain in 1 litre of air to give the same current as that found for the gas.

The dissolved gases were also investigated. Some waters, those from Plombières and Luxeuil, for instance, were found to contain about as much emanation in 10 litres as would be disengaged by 1 mg. of radium bromide in 1 minute. Further, it was observed that the same waters gave a much smaller amount of emanation when examined two months after being collected; this fact shows that the radioactivity which they contain cannot be due to dissolved radium bromide, but must be ascribed to some more remote cause. S. S.

Radioactivity and Matter. CLEMENS WINKLER (*Ber.*, 1904, 37, 1655—1662).—The results obtained by investigators of radioactivity are critically discussed, and a note of caution is sounded against too ready acceptance of supposed new elements. Attention is drawn to the very slight character of the chemical evidence available, and to the fact that radioactivity is invariably associated with uranium. It is suggested that radioactivity may be a purely physical phenomenon, manifesting itself through matter, but without influence on its chemical nature. A parallel case is suggested in the magnetism of ferrosoferric oxide, which can be intensified, transferred, apparently destroyed, and reproduced, like radioactivity; no one, however, supposes that magnetic ferrosoferric oxide contains an element not present in non-magnetic ferric oxide. Only when pure radioactive substances are obtained in larger quantities, and when their chemical behaviour is definitely characterised, can the existence of special radioactive elements be regarded as established. J. C. P.

Emanation Substance. Emanium. FRITZ GIESEL (*Ber.*, 1904, 37, 1696—1699. Compare *Abstr.*, 1903, ii, 193).—According to an investigation of the spark spectrum by Runge and Precht, the emanation substance previously described (*loc. cit.*) consists chiefly of lanthanum with a little cerium. The dehydrated chloride and bromide phosphoresce (the sulphate to a less extent), and show a discontinuous phosphorescence spectrum of three lines, situated at about equal intervals between red and bluish-green. Glass vessels in which the substance has been kept for a few months are coloured violet, so far as the contact has extended. Paper similarly exposed becomes brown and falls to pieces. The activity of the solid salts reaches its maximum about a month after they have been separated from solution, and thereafter remains unchanged (compare the behaviour of radium, *Abstr.*, 1900, ii, 19). This behaviour is characteristic of primarily radioactive elements, and the author accordingly supposes that there is in the "emanation substance" a strongly radioactive element, most

probably allied to lanthanum, for which the name *emanium* is proposed. The slight activity of commercial uranium salts is due more likely to traces of emanium than of radium. The strongly active lead preparations previously described (Abstr., 1902, ii, 208) derived their activity most probably from the emanation substance.

Barium sulphate, precipitated from a solution containing slightly active noble earths, is more strongly active than these. So also the activity of barium bromide containing emanium can be concentrated by fractional crystallisation, as in the case of the barium-radium mixture. This barium bromide, when anhydrous, exhibits strong phosphorescence; its spark spectrum is quite distinct from that of an equally active barium radium bromide. The activity of the best emanium preparations is very great, and the scintillations produced at a zinc blende screen are larger and more distinct than in the case of radium.

J. C. P.

Action of Canal Rays on Zinc Oxide. II. JULIUS TAFEL (*Ann. Physik*, 1904, [iv.], 14, 206—207).—A reply to Schmidt (this vol., ii, 307).

J. C. P.

Reversible Photochemical Reactions in Homogeneous Systems. I. Anthracene and Dianthracene. ROBERT LUTHER and FRITZ WEIGERT (*Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 828—839).—When a boiling solution of anthracene in phenetole is exposed to the light of an arc lamp, dianthracene (m. p. 270—280°) is formed in considerable quantity. On the other hand, when dianthracene is suspended for about 20 hours in boiling phenetole, light being excluded, it is transformed completely into anthracene and is dissolved. Similar results are obtained in boiling anisole and boiling xylene.

The conversion of dianthracene into anthracene when dissolved in phenetole or anisole has been studied quantitatively and found to conform to the equation for a unimolecular reaction.

When boiling solutions of anthracene and dianthracene are exposed to light, a condition of equilibrium is reached in a few hours. The concentration C of the dianthracene at the point of equilibrium is (1) inversely proportional to the square of the distance from the lamp; (2) directly proportional to the relative intensity of the light; (3) proportional to the surface area exposed to the light; (4) from 1 mm. upwards, independent of the thickness of the liquid layer through which the light passes; (5) inversely proportional to the volume or weight of the solution; (6) nearly independent of the anthracene concentration at the point of equilibrium. C varies also with the nature of the illumination, and with the solvent used, but for a given source of light, a given solvent and a given temperature, an empirical formula can be found which gives values of C in good agreement with experiment.

J. C. P.

Spark Potential in Chlorine, Bromine, and Helium. F. RITTER (*Ann. Physik*, 1904, [iv.], 14, 118—128).—The ratios V_{Cl}/V_{air} , and V_{Br}/V_{air} , where V is the spark potential, are not constant, but gradually increase with increasing sparking distance (δ) and increasing gas

pressure (P), ultimately approaching limiting values. The ratio V_{He}/V_{air} , on the other hand, diminishes as δ and P increase, and it is found that the curves obtained by plotting spark potential against sparking distance, which are concave to the horizontal axis for all other gases, are straight lines in the case of helium. These lines cut the vertical axis at the point 300 for all pressures, indicating a constant resistance to be overcome between the helium and the electrode.
J. C. P.

Significance of the Maximum in the Conductivity Curves of Kraus at High Temperatures. HARRY C. JONES (*Amer. Chem. J.*, 1904, 31, 584—585).—An investigation of the conductivity of solutions of electrolytes in methyl and ethyl alcohols has been made recently by Kraus (*Phys. Rev.*, 1904, 18, 40), and it has been shown that the conductivity passes through a maximum with rise of temperature which in the case of solutions in methyl alcohol occurs at 150° and in that of ethyl alcohol solutions at about 100° .

The present paper draws attention to these results, and points out that there are two influences exerted on the conductivity with rise of temperature, namely, an increased rapidity of movement of the ions and a decrease in the association of the solvent. The maximum in the conductivity curve represents the temperature at which these opposite influences become equal.
E. G.

Study of Hydrolysis by Conductivity Methods. JULIUS STIEGLITZ and IRA H. DERBY (*Amer. Chem. J.*, 1904, 31, 449—458).—The proportions of free acid, free base, and salt in aqueous solutions of the hydrochlorides of weak bases can be determined most rapidly by a method based on conductivity measurements. It has been shown by Walker (*Abstr.*, 1890, 5) that in such cases the percentage of salt x which has suffered hydrolysis can be calculated from the observed molecular conductivity, M_v , by means of the equation

$$x = M_v - \mu_v / \mu_{HCl} - \mu_v$$

where μ_v and μ_{HCl} represent the conductivity of the non-hydrolysed salt and the free acid respectively. Various interpretations have been given by different workers to the value of μ_{HCl} in this equation. It is regarded by Walker as representing the molecular conductivity of the acid for the original concentration of the salt solution, that is, for a completely hydrolysed salt, and this view is adopted in the present paper. Experiments have been made to test the trustworthiness and range of accuracy of the equation in the analysis of mixtures of hydrochloric acid and potassium chloride of varying concentrations, but especially $N/32$ solutions of each, and also in the determination of the conditions of equilibrium in solutions of aniline hydrochloride containing an excess of hydrochloric acid.

The results indicate that this method of analysis of hydrolysed solutions can be used successfully in the case of solutions undergoing continuous change and has the advantage of great rapidity. It has been applied to the determination of the velocities of rearrangement and the affinity constants of certain aminophenyl alkyl carbonates (Stieglitz and Upson, this vol., i, 575).
E. G.

Formation of Electrolytic Gas by an Alternating Current.

RALPH G. VAN NAME and LEOPOLD GRÄFENBERG (*Zeit. Elektrochem.*, 1904, 10, 303—309).—The following substances were used as electrodes in the electrolysis of sulphuric acid (20 per cent. H_2SO_4) with a current alternating 110 times per second; carbon, graphite, silicon, lead, tin, platinum, gold, aluminium, and platinum-iridium. The same substances with the exception of the two last and also silver, nickel, iron, copper and zinc, were tried with 28 per cent. potassium hydroxide. Carbon and graphite were pulverised, silicon and aluminium gave large anodic resistances in acid solution, and in alkaline solution silicon was rapidly dissolved. Lead and tin in acid solution and lead, tin, and zinc in alkaline solution were rapidly acted on. With the other metals, the yields of electrolytic gas and the *E.M.F.* required were determined. The yield of electrolytic gas increases with the current density, but since the *E.M.F.* also increases in about the same ratio, the energy efficiency remains approximately constant. Platinum gives the best results, gold being almost as good, but in both cases the surface of the metal is disintegrated and small quantities pass into solution. The disintegration of the surface diminishes the yield of gas. Silver in alkaline solution is less acted on than any other metal tried. Copper, iron and nickel are all oxidised more or less energetically. The largest energy efficiency observed is about one-half of that attainable with direct current; this is mainly due to the very high current density, which must be employed with alternating current (1.7 to 20 amperes per sq. cm.). There appears to be no electrode material which is unacted on under these conditions.

T. E.

Employment of Alternating Currents in Chemistry and the Reactions which they Determine. MARCELLIN BERTHELOT (*Compt. rend.*, 1904, 1130—1133).—The author recalls some experiments made by him in 1879 with the object of ascertaining the effect of an alternating current on solutions of dextrose. The simultaneous oxidation and reduction of the sugar were thus studied, and it was found that alcohol and carbon dioxide were produced; this action may be compared to the alcoholic fermentation of sugar. Other instances quoted are: the oxidation of an aldehyde in alkaline solution in presence of air, the oxidation of silver in presence of sodium chloride and air, and the action of potassium cyanide on platinum recently observed by Brochet and Petit (*Abstr.*, 1904, ii, 229).

S. S.

Concentration of Mercury Ions in the Calomel Electrode and the Solubility of Calomel. HEINRICH LEY and CHR. HEIMBUCHER (*Zeit. Elektrochem.*, 1904, 10, 301—303).—The published values of the solubility of calomel vary from 1×10^{-6} to 6×10^{-6} . The authors find, by the sugar inversion method, that about 3.4 per cent. of the mercurous perchlorate contained in a 0.1*N* solution of that salt is hydrolysed. The electrolytic conductivity of solutions of

barium perchlorate is determined and the assumption made that the dissociation of a solution of mercurous chlorate is the same. In this way, it is calculated that the concentration of the mercurous ions (Hg_2^{++}) in a 0.1*N* solution of mercurous perchlorate is 0.035. The *E.M.F.*'s of cells consisting of combinations of the 0.1*N* and *N* calomel electrodes with a 0.1*N* solution of mercurous perchlorate are then measured; the mean values found are 0.420 and 0.472 volt respectively. From these values, the concentrations of the mercurous ions (Hg_2^{++}) at the electrodes are 2.0×10^{-16} and 3.5×10^{-18} respectively, and assuming the saturated solution of calomel to be completely dissociated, the solubility of calomel is 0.8×10^{-6} . T. E.

Velocities of the Ions in Liquid Ammonia Solutions. EDWARD C. FRANKLIN and HAMILTON P. Cady (*J. Amer. Chem. Soc.*, 1904, 26, 499—530).—A form of apparatus has been constructed by the authors by means of which the absolute velocities of certain ions in liquid ammonia have been determined. The velocities of a number of univalent ions in liquid ammonia at -33° are from 2.4 to 2.8 times as great as they are in aqueous solutions at 18° , and are in agreement with the velocities calculated from conductivity measurements by Kohlrausch's method. Whilst the dissociating power of liquid ammonia is comparatively low, the speed with which the ions migrate is exceptionally high. Experiments were made with solutions of ammonium nitrate, ammonium iodide, potassium nitrate, sodium nitrate, sodium bromate, and silver nitrate, respectively, in liquid ammonia, where the speed of the cation was measured; the speed of the anion was measured with solutions of ammonium nitrate, potassium nitrate, ammonium chloride, sodium nitrate, sodium chloride, ammonium bromide, sodium bromide, ammonium iodide, and potassium iodide respectively. The tabulated results show that the assumption that the speeds of the ions are independent of the degree of dilution is justified in the cases of ammonium nitrate, potassium nitrate, sodium chloride, and sodium bromide. In solutions of ammonium chloride and ammonium bromide, there is obviously a rapid increase in the transport number of the ion with the concentration. The behaviour of ammonium iodide is similar but less marked. A. McK.

Electric Osmosis in Methyl Alcohol. A. BAUDOUIN (*Compt. rend.*, 1904, 1165—1166).—The present communication deals with the influence of polyvalent ions on the charge assumed by the cell-wall in contact with methyl alcohol. The influence of certain univalent ions has already been described (this vol., ii, 380). A polyvalent ion has little or no effect on a similarly charged cell-wall, but if the charge on the latter is of opposite sign to that of the ion, it is diminished, and in some cases reversed. S. S.

Specific Heat of Carbon at High Temperatures. LUDWIG KUNZ (*Ann. Physik*, 1904, [iv], 14, 309—333).—Using a small electrical resistance oven and an ice calorimeter, the author has deter-

mined the specific heat of wood charcoal at temperatures between 400° and 1300°. The following are the values obtained:

| | | | |
|------|-------|------|-------|
| 435° | 0.243 | 928° | 0.359 |
| 558 | 0.290 | 932 | 0.358 |
| 564 | 0.290 | 1059 | 0.362 |
| 716 | 0.331 | 1192 | 0.376 |
| 739 | 0.324 | 1202 | 0.380 |
| 920 | 0.357 | 1297 | 0.381 |
| 921 | 0.359 | | |

These values are not very different from those given by Weber for graphite.
J. C. P.

A New Pyrometer. CHARLES FÉRY (*Bull. Soc. chim.*, 1904, [iii], 31, 701—702. Compare Abstr., 1903, ii, 124 and 293).—The apparatus consists of a lens made of a diathermanous substance, such as rock-salt or fluorspar, bearing cross-wires—one of iron and the other of “constantan” (an alloy of copper and nickel), which together constitute a thermo-electric couple. The current generated by the exposure of this to the radiation from the source of heat is measured by a galvanometer. For industrial purposes the lens may be of glass, and the instrument is then graduated by comparison with one having a lens of rock-salt.
T. A. H.

Boiling Points of Homologous Compounds. HUGH RAMAGE (*Proc. Camb. Phil. Soc.*, 1904, 12, 445—448).—To connect the boiling points and the molecular weights of the fatty hydrocarbons, the author suggests the formula $T = a[M(1 - 2^{-n})]^{\frac{1}{2}}$, where n is the number of carbon atoms in the molecule. The constant a is the same as in the similar formula brought forward by Walker (*Trans.*, 1894, 65, 193, 725), but it is also given by the expression $a = 23.5P^{.07}$, where P is the pressure. Walker's formula is not valid over such a wide range as the author's formula, by which the boiling points of the hydrocarbons from methane to hexadecane may be calculated with a maximum error of 3.9° in the case of propane.

The boiling points of the first eight members of the normal alcohol series may be calculated by the formula $T = 286.2 + 1.41 M$; the errors are small, except in the case of methyl alcohol.

For the boiling points of aldehydes the equation $T = 209.14 + 1.9286 M$ may be used; for ketones the equation $T = 250.07 + 1.4643 M$.
J. C. P.

Sydney Young's Law of Distillation. (Miss) J. REUDLER (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 6, 807—809).—Young's law of fractional distillation (*Trans.*, 1902, 81, 752) is criticised and experimentally tested with a mixture of benzene and aniline, which presents a mixture with a very steep Tx -line. The conclusion is drawn that Young's rule is a proof of the excellent way in which Young's still-heads work, but that, from the point of view of quantitative analysis, this rule must only be taken as an application of the

most obvious operation, namely, that of separating a substance in the pure state from a mixture and then weighing it separately.

A. McK.

A New Dephlegmator for Fractional Distillation and for Reflux Distillation. JOSEF HOUBEN (*Chem. Zeit.*, 1904, 28, 525—527).

—An improved form of Winssinger's apparatus.

A. McK.

Heats of Combustion of Some Organic Compounds. EMIL FISCHER and FRANZ WREDE (*Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 687—715).—The author's experiments have been made with a slightly modified Berthelot bomb, the heat capacity of which, along with the calorimeter, has been determined by an electrical method. The substances employed were of a high degree of purity, and details of their preparation and purification are given in the paper. The following numbers represent the molecular heats of combustion at constant volume in Cal.; benzoic acid, 775.3; naphthalene, 1237.5; sucrose, 1363.9; phenylacetic acid, 933.4; glycine, 234.1; alanine, 390.3; leucine, 858.5; glycine anhydride, 476.7; alanine anhydride, 788.4; leucinimide (3:6-diisobutyl-2:5-diketopiperazine), 1726.2; glycylglycine, 472.4; glycylglycine ethyl ester, 805.3; glycylglycinecarboxylic acid, 473.7; α -carbethoxyglycylglycine ethyl ester, 1123.2; β -carbethoxyglycylglycine ethyl ester, 1094.8; leucylglycylglycine, 1335.9; isoserine (β -aminolactic acid), 344.5; aspartic acid, 387.1; glutamic acid, 544.2; phenylglycine, 957.8; anilinoacetic acid, 967.9; benzoylaminocinnamic anhydride, 1858.3; benzoylaminocinnamic acid, 1854.5; benzoylphenylalanine, 1895.9; phenylalanine, 1114.1; barbituric acid, 360.7; diethylbarbituric acid, 985.9; silk fibroin, 5167.9 (cal. per gram); 4-methyluracil, 567.7; 5-methyluracil (thymine), 566.4; 4-methylhydrouracil, 619.6; phenyluracil, 1134.9; hexoic acid, 839.6; hydrosorbic acid, 797.0; sorbic acid, 745.9. The heats of combustion of twelve of these compounds have been previously determined, chiefly by Stohmann, Berthelot, and his pupils. In most of these cases there is a satisfactory agreement between the authors' values and the earlier ones. From eight pairs of compounds in the foregoing list, it is shown that the molecular heat of combustion increases by 155.9—158.1 Cal. for each addition of CH_2 . Similarly, the increase in the molecular heat of combustion for an addition of 2H is found in five cases to be respectively 41.4, 51.9, 42.6, 45.6, and 48.6 Cal. The increase of the heat of combustion for 2H is greater in the pair sorbic acid—hydrosorbic acid than in the pair hydrosorbic acid—hexoic acid, a result that agrees with Thiele's views (*Abstr.*, 1899, i, 554). The increase of the heat of combustion corresponding with the introduction of the NH_2 group is found in three cases to be 24.4, 28.6, 29.3 Cal. The introduction of the phenyl group means an increase of 723.8 Cal. in the heat of combustion. The thermal value of the anhydride formation in the case of the amino-acids indicates that the formation of these polypeptides and diketopiperazines from amino-acids is accompanied by absorption of heat. The difference between the heats of combustion for isomerides is specially noteworthy in the case of α - and β -carbethoxyglycylglycine ethyl esters.

J. C. P.

Temperature Variation of the Coefficient of Expansion of Pure Nickel. E. PHILIP HARRISON (*Phil. Mag.*, 1904, [vi], 7, 626—634).—Between 365° and 370°, the coefficient of thermal expansion of pure nickel wire undergoes a sudden change, which is of the same magnitude and occurs at the same temperature whether the temperature of the wire is rising or falling. The change is not modified by successive heatings and coolings, neither is the wire permanently elongated. The wire was heated by a current and its temperature was deduced from its electrical resistance. J. C. P.

Density of Aqueous Salt Solutions Considered as Additive Properties of the Ions, the Existence of Hydrated Ions. P. VAILLANT (*Compt. rend.*, 1904, 138, 1210—1213).—If at t° , s_0 be the density of water, S that of an aqueous solution containing n gram-equivalents of a substance of equivalent E , k the number of equivalents of water associated with each equivalent of the dissolved substance, ϕ the volume per gram-equivalent of the hydrate in solution, N the number of equivalents of water per litre of the solution, then $(E + k \times 9)/s_0 - \phi = 1000(s/s_0 - 1)/n = A$. From a consideration of the values of A for various ions, the following conclusions are drawn; (1) two ions unite to form an electrolyte without any appreciable contraction; (2) in general the ions are anhydrous ($k=0$). The polyvalent ions have a small volume ($E-A$) and a large density $E/(A-E)$; the univalent anions have a density of about 5, the univalent cations a density of about 2; hydrogen, lithium, and ammonium are exceptions, the density of the first being about $\frac{1}{11}$, and of the two last $\frac{2}{3}$; (3) in the case of the cations OH ; F ; $\frac{1}{2}\text{S}$; $\frac{1}{2}\text{CO}_3$, k is not zero, that is, the ions are hydrated, the residual valencies of the oxygen, sulphur, or fluorine atom uniting with the oxygen of the water molecule to form a hydrated ion of the type $\text{H}_2\text{O}:\text{O} < \text{H}$.

M. A. W.

Studies in Viscosity. CHARLES E. FAWSITT (*Electro-Chem., Metall.*, 1904, 3, 664—668).—The viscosity η of a solution containing several non-electrolytes is given by the equation $\eta = A^x B^y C^z \dots$, where x, y, z, \dots are the concentrations of the substances with viscosity constants $A, B, C \dots$. Extending this relationship to electrolytes, the author shows that if a strong base XOH and a strong acid HY could be mixed in equivalent quantities without chemical action taking place, the viscosity would be given by the product $\eta_{\text{H}^+} \times \eta_{\text{X}^-} \times \eta_{\text{Y}^-} \times \eta_{\text{OH}^+}$. Actually, the viscosity is given by $\eta_{\text{X}^-} \times \eta_{\text{Y}^-}$, and if this is divided into the calculated product just referred to, the value of $\eta_{\text{H}^+} \times \eta_{\text{OH}^+}$ is obtained. The value should be independent of the particular base and acid used, so long as they are both strong, and the author shows that this is very nearly the case when $N/2\text{HCl}$ is neutralised by sodium hydroxide, potassium hydroxide, or tetramethylammonium hydroxide. Further, the value of $\eta_{\text{H}^+} \times \eta_{\text{OH}^+}$ thus obtained agrees with the product of the viscosity values for H^+ and OH^+ in $N/2$ solution (see Euler, *Zeit. physikal. Chem.*, 1898, 25, 536). When a weak base is used to neutralise the strong acid, the above simple relation does not hold.

From experiments recorded in an earlier paper (this vol., ii, 323), and supplemented by later work, it appears that the viscosities of solutions of carbamide hydrochloride, and dimethylcarbamide hydrochloride are very nearly the same respectively as the values of the product $\eta_{\text{amide}} \times \eta_{\text{HCl}}$.

Experiments with (1) carbamide, methylcarbamide, ethylcarbamide, dimethylcarbamide; (2) acetamide, propionamide, and butyramide, have shown that the viscosity of molecular solutions is in the main an additive property.

J. C. P.

Does the Application of Tyndall's Optical Method permit of the Demonstration of the Presence of Molecules in Solutions?

CORNELIS A. LOBRY DE BRUYN and LUDWIG K. WOLFF (*Rec. trav. chim.*, 1904, 23, 155—168. Compare Abstr., 1900, ii, 136; 1902, ii, 646).—The authors review the work of Picton and Linder (*Trans.*, 1892, 143), Spring (Abstr., 1899, ii, 537 and 585; 1900, ii, 713; 1901, ii, 297), Stoeckel and Vanino (Abstr., 1900, ii, 11), Zsigmondy (Abstr., 1898, ii, 522; 1900, ii, 397), Billitzer (this vol., ii, 18), and Muller (this vol., ii, 18) in its bearing on this subject. They have repeated Spring's experiments (Abstr., 1899, ii, 585) with various inorganic salts and organic substances, the solutions being clarified by precipitating zinc hydroxide or ferrocyanide in them. In order to avoid errors due to fluorescence, yellow light was employed. Under these conditions, solutions of inorganic salts in water showed no internal reflection and this was also true of carbamide, acetamide, and methyl and ethyl alcohols dissolved in water; on the contrary, solutions of sucrose and raffinose exhibited a slight internal reflection of polarised light, as did also phosphomolybdic acid. In the last case, the luminescence was probably in part due to hydrolytic dissociation, since, after a time, solutions of this material deposit molybdic acid. Organic substances of high molecular weight, such as stearin and the benzoic esters of mannitol, dulcitol, and raffinose, dissolved in organic solvents, were more luminescent than the solvents themselves. From these results, the authors conclude that in the case of substances of complex molecular structure the internal reflection of light in solutions may be due to diffraction of light by the molecules of the substance and that the phenomenon is not confined to substances, such as colloids, existing in "pseudo"-solution. This implies that there is continuity, so far as regards this phenomenon, between "true" and "pseudo"-solution.

T. A. H.

Variations in Concentration of Solutions and the Crystallisation of Dissolved Substances under the Influence of "Centrifugal" Force.

R. P. VAN CALCAR and CORNELIS A. LOBRY DE BRUYN (*Rec. trav. chim.*, 1904, 23, 218—223).—Gay-Lussac had observed that the influence of gravity did not induce unequal concentration in solutions, and, later, Gouy and Chaperon pointed out that this negative result was probably due to the feeble character of the force employed (Abstr., 1887, 1013). Courbes and subsequently Bredig (Abstr., 1895, ii, 490) had pointed out that "centrifugal" force

should produce the same effect as gravitation in experiments of this kind, and the latter effected by this means the separation of hydrogen and hydrogen iodide. Experiments of this type with solutions have already been made or suggested by Colley, van't Hoff, and Quincke.

The authors employed a rotating drum with a cover carrying four test-tubes, one at the centre and the others placed at different distances from this; these could be closed simultaneously by four rubber bungs, supported on a copper wire attached to a disc which could be moved along the longitudinal axis of the drum. By this means, samples of the liquid could be taken simultaneously at four different points in the cross section of the drum.

Solutions of potassium thiocyanate, ferrocyanide, and iodide, and of sucrose in water, were employed and in each case it was found possible to induce unequal concentration of the solution. Thus in the case of a solution of sucrose having originally a rotation of 46.8° , after being whirled at the rate of about 2000 revolutions per minute during four hours, the sample collected in the tube nearest to, but not at the centre of, the drum had a rotation of 41° , that in the next tube 51.5° , and that in the peripheral tube 47° . Normally, the most concentrated solution should be found in the peripheral tube; the abnormality in the present instance is due to the production of a wave over the third tube when the disc is moved to enable the samples to be taken. Using a solution of sodium sulphate in water saturated at 9° , 3.75 per cent. of the salt was separated as the solid decahydrate by rotating the drum at the rate of about 2400 revolutions per minute for a period of five hours.

T. A. H.

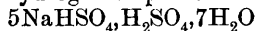
Gelatinisation. III. Internal Friction of Colloidal Solutions. S. A. LEVITES (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 401—417. Compare Abstr., 1902, ii, 312, and 1903, ii, 641).—The author has investigated the relation between the changes brought about in (1) the velocity of coagulation of solutions of gluten, agar-agar, albumin, and casein (in alkali) by the addition to them of various substances and (2) the internal friction of the solutions. The results lead to the following conclusions. Colloidal liquids may be regarded as solutions, inasmuch as they consist of homogeneous mixtures of a liquid and a solid phase. Among solutions of colloids, those of organic colloids are most nearly allied to actual solutions; metallic hydrosols are most probably pseudo-solutions. A jelly consists of a mixture of a solid and a liquid phase. Gelatinisation does not take place simultaneously with the attainment of equilibrium between these two phases, which only sets in very gradually after gelatinisation. The speed of gelatinisation in presence of a foreign substance depends on the influence exerted by that substance on the solubility of the colloid in question. The influence exerted by a foreign (crystalloid) substance on the internal friction of a colloidal solution depends on the influence of the substance on the internal friction of the solvent, but is independent of the nature of the colloid. More complex results are obtained when two or more colloids are present in one and the same solution.

T. H. P

Decomposition of Some Acid Sulphates as the Result of Mechanical Deformation. WALTHER SPRING (*Rec. trav. chim.*, 1904, 23, 187—201. Compare this vol., ii, 313).—In conformity with the view previously expressed (*loc. cit.*) that substances under compression assume to some extent the properties of the liquid state, the author finds that under compression involving mechanical deformation, compounds which may be regarded as resulting from the combination of a solid with a liquid tend to decompose into these generators. The present series of experiments is confined to the anhydrous and hydrated sulphates of the alkali metals. The compression was effected in a steel cylinder, the bottom of which was perforated with a single small hole to permit liquid to flow away and provided with a loosely-fitting piston between which and the walls of the cylinder the salt could "flow."

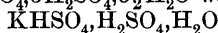
Lithium hydrogen sulphate was found to have the sp. gr. 2.123: when compressed there was a visible formation of sulphuric acid, and the composition of that portion of the salt which had "flowed" was approximately represented by the formula $9\text{LiHSO}_4, 2\text{H}_2\text{SO}_4$. The monohydrated salt behaved similarly, and the solid residue left in the cylinder in this case contained 10.8 per cent. of lithium as against 5.85 per cent. present in the original monohydrate.

Sodium hydrogen sulphate was found to have the sp. gr. 2.435 at 13° as against 2.742 found by Playfair and Joule. When compressed, no decomposition occurred. The monohydrate had the sp. gr. 2.103 at 13.5° , and under compression at 10° decomposed very slightly if at all, but lost 64.5 per cent. of its water of crystallisation when compressed at 40° . The salt $6\text{NaHSO}_4, \text{H}_2\text{SO}_4, 16\text{H}_2\text{O}$ liberated sulphuric acid and water under compression at 10° , and was almost completely converted into anhydrous sodium hydrogen sulphate. The salt



was converted into NaHSO_4 by compression at 40° , and the salt $5\text{NaHSO}_4, \text{H}_2\text{SO}_4, 3\text{H}_2\text{O}$ into $5\text{NaHSO}_4, \text{H}_2\text{SO}_4$ by compression at 16° and into NaHSO_4 at 80° , whence it appears that water is eliminated before sulphuric acid under these conditions.

Anhydrous potassium hydrogen sulphate (sp. gr. 2.302 at 13°) and the corresponding salts of caesium (sp. gr. 3.352 at 16°) and rubidium (sp. gr. 2.892 at 16°) underwent no change even when compressed at 100° , but the salt $2\text{KHSO}_4, 3\text{H}_2\text{SO}_4, 3\frac{1}{2}\text{H}_2\text{O}$ was converted into



by compression at the ordinary temperature.

When a mixture of sodium hydrogen sulphate with cupric oxide was subjected to simple compression, no combination occurred; but when mechanical deformation accompanied the compression, a mixture of sodium and cupric sulphates was formed. A similar change was to some extent produced by simply grinding the two substances together in a mortar.

It is pointed out that these observations may furnish an explanation of the variations observed in the composition of certain rocks.

T. A. H.

The Equations of Clausius and van der Waals for the Mean Length of Path and Number of Collisions. PHILIPP KOHNSTAMM (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 6, 787—793).—**Van der Waals' Equation of State.** PHILIPP KOHNSTAMM (*ibid.*, 794—807).—Mathematical ; unsuitable for abstraction. A. McK.

Crystallisation in Three Component Systems. WILLIAM C. GEER (*J. Physical Chem.*, 1904, 8, 257—287).—The three-component system is studied with the main object of determining the composition of the phases which separate when ternary systems are cooled. The locus of the points representing the composition of the liquid during cooling until the quintuple point is reached, is called the crystallisation curve, and the author shows this is a straight line until a boundary curve is reached which it follows. Of these boundary curves, two types exist : along one, two phases separate together ; along the other, one phase separates whilst the second disappears : and both types are discussed. Numerous diagrams are given in the paper to illustrate the course of the curves. The conclusions drawn are illustrated by data taken from various systems which have been previously investigated, namely, the systems copper chloride, potassium chloride and water, potassium sulphate, magnesium sulphate and water, ferric chloride, hydrogen chloride and water ; and gold, cadmium, and tin. L. M. J.

The Ternary System: Benzene, Acetic Acid, and Water. AZARIAH T. LINCOLN (*J. Physical Chem.*, 1904, 8, 248—256).—The author has previously shown that the equilibrium of the system benzene, water, and alcohol is in complete accord with the mass law equation. Waddell, however, has found that the system benzene, acetic acid, and water does not yield equilibria in accord with the mass law (*Abstr.*, 1899, ii, 144) ; the author has therefore repeated Waddell's work, taking the utmost precaution to ensure purity in the reagents and to obtain the exact composition of equilibrium at the definite temperature required. He shows that Waddell's method of always working to the same degree of cloudiness is an inexact one, and that the first trace of opalescence must be taken. His results are in good accord with the mass law, the values being represented by the equation $n \log x + \log y = \log C$, where x and y represent the quantities of benzene and water per 5 c.c. of acetic acid. It is also shown that two sets of equilibria occur according to which non-miscible liquid separates, so that if curves are drawn for $\log x$ against $\log y$, the curve consists of two straight lines. The values of n are proved to be independent of temperature, this being in accord with the theory. L. M. J.

The Beckmann Rearrangement. Velocity of Transformation of Acetophenoneoxime into Acetanilide. CORNELIS A. LOBRY DE BRUYN and C. H. SLUITER (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 6, 773—778).—Additive compounds as intermediate products have occasionally been isolated during a Beckmann rearrangement, those

compounds containing a negative group (or the group OK) attached to the nitrogen atom, which group then changes place with the alkyl or aryl group attached to the carbon atom. The hydroxyl group itself does, however, occasionally replace the negative group referred to.

The Beckmann rearrangement has now, for the first time, been subjected to a dynamical investigation, the transformation studied being that of acetophenoneoxime into acetanilide under the influence of sulphuric acid. The amount of acetanilide in a mixture of it with unchanged oxime, may be estimated by hydrolysing it by boiling for a few hours and then distilling off the acetic acid and titrating it. The velocity with which the anilide is formed may accordingly be determined.

The reaction is unimolecular. The transformation velocity increases with the concentration of the acid. The influence of temperature was also examined.

A solution of sulphur trioxide in chloroform does not cause any transformation of the oxime.

The Beckmann rearrangement is an intramolecular change. If the addition of sulphuric acid causes the formation of an intermediate compound, this formation must occur with immeasurably great velocity.

The views advanced by Stieglitz as to the mechanism of the Beckmann rearrangement are adversely criticised. A. McK.

Ferment Action. LEO LIEBERMANN (*Ber.*, 1904, 37, 1519—1524).—Colloidal solutions of platinum contain "active" oxygen, which may be detected by means of potassium iodide and starch, *p*-phenylenediamine or indigo solution. The action of hydrogen or nitrogen on the solution causes a diminution of the amount of the active oxygen, whilst the exclusion of air or oxygen entirely prevents the solutions responding to the foregoing tests. Hydrogen and nitrogen affect the colloidal solutions in a different way, the former changing the brownish shade of the solution to blackish-brown. In certain circumstances, the foregoing gases may enhance the catalytic activity of the solutions with regard to hydrogen peroxide, probably by increasing the number of the platinum particles. On boiling, the colloidal solutions lose their active oxygen and, at the same time, their power of decomposing hydrogen peroxide, although no separation of platinum occurs; if the solutions are allowed to cool in air or oxygen they gradually regain their activity, but in an atmosphere of hydrogen or nitrogen this recovery is much retarded. The author considers, contrary to Bredig's view (*Abstr.*, 1900, ii, 213), that the first phase in the catalytic decomposition of hydrogen peroxide is the formation of an oxide of platinum by the intervention of atmospheric oxygen, and that the hydrogen peroxide reduces this, forming molecular oxygen, which again combines with platinum.

A number of "catalases" of vegetable and animal origin were found neither to contain "active" oxygen nor to possess the power of rendering oxygen active. On the other hand, most were able to absorb ozone in such a way that its presence in solution could be

detected; air, oxygen, hydrogen, and nitrogen did not affect their catalytic activity. The mechanism of the decomposition of hydrogen peroxide by these ferments differs essentially from that caused by colloidal platinum; a direct action on the peroxide must be assumed, which produces an unstable "ferment-oxide" similar to that formed by ozone.
W. A. D.

Pseudo-Acids. JAN VON ZAWIDZKI (*Ber.*, 1904, 37, 2298—2301. Compare Kauffmann, this vol., ii, 326).—Basing his argument on the law of mass action, the author shows that the "apparent" dissociation constant (k_a), calculated from the electrical conductivity of a pseudo-acid, must be smaller than the "real" dissociation constant (k_i) unless isomerisation is complete. The constant $k_1 = \frac{k_{H_2O}}{k}$, where k is the constant of hydrolysis of the sodium salt. The isomerisation constant (k_2) of the pseudo-acid is calculated from the equation $k_2 = k_a/(k_1 - k_a)$.
G. Y.

Laws of Formation of the Chemical Elements. B. N. TSCHITSCHERIN (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 359—401).—The author develops mathematically the system of the chemical elements, based on experimental data previously developed by him (*J. Russ. Phys. Chem. Soc.*, 1888, 1889, and 1892).
T. H. P.

New Method for the Exact Determination of the Molecular Weights of the Permanent Gases; Atomic Weights of Hydrogen, Carbon, and Nitrogen. PHILIPPE A. GUYE (*Compt. rend.*, 1904, 138, 1213—1215).—The author finds that the value of R , calculated from the relation $V_m(1+a)(1-b) = R$ (compare Guye and Friderich, *Abstr.*, 1900, ii, 709; 1902, ii, 599), varies between 22412 and 22420 for the gases hydrogen, nitrogen, oxygen, and carbon monoxide; if, however, the correction mT_c (where $m = 0.085$) be applied to R , the relation $V_m(1+a)(1-b) = R + mT_c$ can be used to calculate the molecular weights of the permanent gases, for $m = \frac{L}{1000} \frac{R + mT_c}{(1+a)(1-b)}$, where L is the weight in grams of 1 litre of the gas at 0° and under 1 atmosphere pressure. Using the values of L obtained by Morley (as recalculated by Guye and Mallet, this vol., ii, 392) for hydrogen and oxygen, and by Rayleigh for nitrogen and carbon monoxide, the following atomic weights are obtained: H = 1.00765; O = 16.00; N = 14.004; C = 12.003.
M. A. W.

Valency and the Periodic System. Attempt to formulate a Theory for Molecular Compounds. RICHARD ABEGG (*Zeit. anorg. Chem.*, 1904, 39, 330—380).—The distinction between stable compounds which readily suffer dissociation and those which do not, is one of degree. In connection with the relationship between "affinity" and valency, it is pointed out that the affinity of the different valencies of an atom cannot be alike, otherwise such a change as, for example, the conversion of ferric into ferrous chloride could not take place. An attempt is made to formulate a theory for molecular compounds on the

basis of varying valency of the elements (compare Abegg, Abstr., 1903, ii, 536). When one valency is satisfied in the case of a polyvalent atom, where initially the valencies were alike, the residual valencies are weakened; the difficulty with which the second hydrogen ion in a dibasic carboxylic acid is split off is analogous. Chemical compounds, where the formation of ions cannot be detected, are held together by something of the nature of electro-affinity. The manner in which traces of ionisation of a compound may be detected is indicated. Certain elements are amphoteric in character; thus, hydrogen, boron, silicon, phosphorus, arsenic, antimony, sulphur, and iodine exhibit either positive or negative electro-affinity, according to the nature of the other elements present. The positive electro-valency is more in evidence with the heavier elements of the one group; as, for example, where the elements in question are regarded as the positive portion of the molecule and are combined with the negative portion: thus, nitrogen forms only a trichloride, whilst the specifically heavier phosphorus forms both a tri- and penta-chloride. Other instances are quoted with reference to the variation of affinity with the size and polarity of the atom. The hypothesis of "normal" and "contra"-valencies is further developed. Chlorine possesses one negative normal valency and seven positive contra-valencies, whilst silver possesses one positive normal valency and seven (hypothetical) contra-valencies. The variation of valency in the different groups is indicated as follows:

| | Group: | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|----------------------|--------|------|------|------|----|----|----|----|
| Normal valencies ... | | +1 | +2 | +3 | +4 | -3 | -2 | -1 |
| Contra-valencies ... | | (-7) | (-6) | (-5) | - | +5 | +6 | +7 |

Under the heading of molecular compounds the author discusses associated compounds and others such as complex salts and hydrates. The decomposition of a polymeric compound, such as cyanuric acid, at an elevated temperature, indicates that polymeric compounds may also be included under the compounds commonly termed molecular.

The greater the number of contra-valencies possessed by any particular element, the greater the tendency to the formation of molecular compounds in which the element is contained. Solutions may also be included in the same category as molecular compounds. The capability of a metal to appear in the neutral portion of a complex anion or as a single ion of a complex cathion is an expression of its negative contra-valency. A. McK.

Characterisation of Flame. NICOLAE TECLU (*J. pr. Chem.*, 1904, [ii], 69, 359—361).—A current of coal-gas is passed into the centre tubulure of a three-necked Woulf's bottle, the two side tubulures of which are fitted with jets so arranged as to allow of variations in the length of the gas columns between the bottle and the flames. It is found that, if the gas pressure be sufficiently diminished, the flames vary in length with their relative heights above the bottle. If the current is stopped, the lower flame is first extinguished, extremely small differences in height causing this. If the openings of the jets are different, the jet with the larger opening must be raised above the other to produce similar flames. G. Y.

A New Mercury Air-Pump. FRITZ W. J. BOEKHOUT (*Chem. Zeit.*, 1904, 28, 459—460).—A new mercury air-pump is described. It has the advantage of being less liable to breakage than the Töpler pump.
A. McK.

[Lecture Experiment.] **Preparation of an Explosive Mixture of Hydrogen and Oxygen.** NICOLAE TECLU (*J. pr. Chem.*, 1904, [ii], 69, 362—364).—The author describes an apparatus for mixing hydrogen and oxygen in the proper proportion for an explosive mixture for lecture experiments.
G. Y.

[Lecture Experiment.] **Electrolysis of Water.** NICOLAE TECLU (*J. pr. Chem.*, 1904, [ii], 69, 364—365).—A modification of the usual lecture apparatus for demonstrating the electrolysis of water is figured.
G. Y.

Inorganic Chemistry.

Decomposition of Hydrogen Peroxide under the Influence of Radium Bromide. HENRY J. H. FENTON (*Proc. Camb. Phil. Soc.*, 1904, 12, 424—426).—The velocity coefficient for the decomposition of hydrogen peroxide in paraffin-coated vessels, calculated from the expression for a unimolecular reaction, gradually increases as the peroxide concentration diminishes. In glass vessels the decomposition velocity is irregular at first, but becomes approximately constant after a few days. The velocity of decomposition, either in glass or paraffin-coated vessels, is approximately doubled under the influence of radium bromide. J. C. P.

Boiling Oxygen. A. BESTELMEYER (*Ann. Physik*, 1904, [iv], 14, 87—98).—A study of the extent of possible superheating in boiling oxygen. The results obtained make it probable that previous determinations of the boiling point of oxygen, in which the thermometer was immersed in the liquid, are a few tenths of a degree too high. On the other hand, the author's results are in harmony with the determinations of Travers, Senter, and Jaquerod (*Abstr.*, 1903, ii, 9), who used a statical method. J. C. P.

The Melting Points of Oxygen and Nitrogen. TADEUSZ ESTREICHER (*Bull. Acad. Sci. Cracow*, 1903, 831—844).—The melting point of oxygen was determined with a helium thermometer; it was found to be approximately -227° . The vapour pressures of melting oxygen, nitrogen, and atmospheric nitrogen were determined by solidifying these gases in a closed vessel connected with a mercury manometer. When the solids were allowed to melt slowly, the pressure, at first zero, gradually rose to a value which remained constant

until complete liquefaction had taken place. In this way, the vapour pressure of melting oxygen was shown to be 0.9 mm., that of melting nitrogen 93.5 mm., and atmospheric nitrogen 90.2 mm. The vapour pressures of nitrogen at temperatures near the melting point have already been determined (Fischer and Alt, *Münchener Akad.*, 1902, 209); with the aid of Ramsay and Young's method, these values may be used to calculate the temperature of nitrogen corresponding with any vapour pressure. Accordingly, the temperature of nitrogen which exerts a pressure of 93.5 millimetres is found to be -210.24° (this figure represents the melting point of pure nitrogen); similarly, atmospheric nitrogen is shown to melt at -210.47° . The difference between the two values, 0.23° , is the lowering in the freezing point of liquid nitrogen which is exerted by the argon in atmospheric nitrogen (1.70 grams per 100 grams of nitrogen). In this way, the author calculates the molecular depression of freezing point of liquid nitrogen and finds it to be 5.39, whence the latent heat of fusion equals 14.49 cal. or 60.44 Joules. S. S.

Heat of Vaporisation of Oxygen and Sulphur Dioxide. TADEUSZ ESTREICHER (*Bull. Acad. Sci. Cracow*, 1904, 183—196).—The method consists in measuring the volume of gas liberated by a known amount of heat which is generated in a platinum resistance wire immersed in the liquid. The quantity of electricity passing through the resistance during the experiment was determined by means of a silver voltameter, and the difference of potential between the ends of the wire was measured with a standardised voltameter.

In measuring the volume of the gas liberated, a correction must be applied for the normal evaporation which takes place without heating the platinum wire. The sulphur dioxide employed was prepared by dropping concentrated sulphuric acid into a strong solution of sodium sulphite. The heat of vaporisation of liquid sulphur dioxide at its boiling point (10.1°) was found to be 96.2 cal. per gram; a value which agrees very closely with that obtained by Mathias (*Abstr.*, 1888, 773), 96.19 at the same temperature.

The oxygen was prepared from potassium chlorate, and was washed with potassium hydroxide before use. The latent heat of vaporisation of liquid oxygen is 58.0 cal. per gram. S. S.

Ozone Apparatus. W. ELWORTHY (*Chem. Centr.*, 1904, i, 1313—1314; from *Electrochem. Zeit.*, 11, 1—5).—In the apparatus described, the silent discharge takes place between spirals of aluminium. The air does not require to be cooled by water, the temperature being kept sufficiently low by employing a rapid stream which is made to pass twice through the field of discharge by means of concentric glass tubes. The air is not specially dried. The apparatus comprises a battery of 10 tubes together with other accessories. By employing an alternating current at 130 volts raised to 11,000—12,000 volts by means of a transformer, 70 grams of ozone per kilowatt-hour are obtained, and the concentration of the ozone reaches 0.4—0.5 gram per cubic metre. E. W. W.

Formation of Ozone at High Temperatures. J. K. CLEMENT (*Ann. Physik*, 1904, [iv], 14, 334—353).—Since the stability of endothermic substances increases as the temperature rises, it is to be expected that at high temperatures oxygen is converted, partly at least, into ozone. Attempts to realise this, in which oxygen was rapidly passed over the electrolytic glow body of a Nernst lamp, were unsuccessful, and no ozone could be detected. So long as traces of nitrogen were present in the oxygen, nitric oxide was produced, a substance the behaviour of which in small concentrations is very similar to that of ozone. The formation of ozone at high temperatures has been recorded by earlier workers, but it is probable that the reactions observed were those of nitric oxide, since no care was taken to exclude nitrogen. Ozone is certainly produced by an electric spark, but this result may be attributed to the action of ultraviolet light.

The author has further studied the rate of decomposition of ozone at higher temperatures. A current of ozonised oxygen, obtained by electrolysis of sulphuric acid, was passed through a vessel kept at a constant temperature, the amounts of ozone before and after the passage of the gas being determined by absorption in potassium iodide and subsequent titration with thiosulphate. The reaction is bimolecular, as found also by Warburg (*Abstr.*, 1902, ii, 130), and van't Hoff's equation for the change of velocity coefficient with temperature represents the experimental results very satisfactorily. It may thus be shown that at 1000° the percentage of ozone in oxygen would fall from 1.0 to 0.001 in 0.0007 second. Hence, even if ozone is formed in quantity at a temperature of about 2200°, it must be decomposed during even the most rapid cooling. J. C. P.

Action of Sulphuryl Chloride on Metallic Oxides. E. SPELTA (*Gazzetta*, 1904, 34, i, 262—267).—Sulphuryl chloride and lead oxide do not react, even when heated together at 140—150° in a sealed tube for several hours.

With lead peroxide, however, sulphuryl chloride readily reacts, sometimes with explosive violence, according to the following equation: $2\text{PbO}_2 + \text{SO}_2\text{Cl}_2 = \text{PbSO}_4 + \text{PbCl}_2 + \text{O}_2$. If the sulphuryl chloride is in slight excess, and the mixture becomes heated above its boiling point, chlorine is also evolved.

With mercuric oxide prepared in the dry way, sulphuryl chloride does not react even on prolonged heating. With yellow mercuric oxide (2 mols.), however, sulphuryl chloride (1 mol.) readily reacts at 150° in a closed tube: $2\text{HgO} + \text{SO}_2\text{Cl}_2 = \text{HgSO}_4 + \text{HgCl}_2$. If the sulphuryl chloride is in excess, sulphur trioxide is also formed, according to the equation: $\text{HgO} + \text{SO}_2\text{Cl}_2 = \text{HgCl}_2 + \text{SO}_3$.

From these reactions it is seen that sulphuryl chloride, which is readily formed from sulphur dioxide and chlorine, is also readily resolved into these components, the change being hence a reversible one. The chlorinating action of sulphuryl chloride must be due to a slightly stable linking between the sulphur dioxide and chlorine, a linking which must have a special form, since its rupture takes place preferably in presence of elements having an electro-positive character.

T. H. P.

Electrolytic Oxidation of Sulphites and Electrochemical Formation of Dithionate. ALFRED FRIESSNER (*Zeit. Elektrochem.*, 1904, 10, 265—289).—In neutral or alkaline solutions, the sulphites of the alkali metals are not reduced at the cathode; at the anode they are oxidised, partly to sulphate, partly to dithionate, $2\text{Na}_2\text{SO}_3 + \text{O} + \text{H}_2\text{O} = \text{Na}_2\text{S}_2\text{O}_6 + 2\text{NaOH}$. Dithionate is not formed under any conditions when the solution is acid, the only product formed at the anode being sulphate; at the cathode, however, hyposulphite and thio-sulphate are produced. The formation of dithionate in neutral or alkaline solutions is found to be conditioned by the potential of the anode. By polarising the (platinum) anode anodically in a solution of sodium hydroxide before use, the formation of dithionate is insured, whereas a cathodically polarised or a depolarised electrode gives no dithionate. These remarks apply to platinised platinum anodes: a smooth platinum anode soon becomes polarised in the sulphite solution itself sufficiently to produce dithionate even if it is initially depolarised. The formation of dithionate is favoured by a rise of temperature to 60—70°; it is practically unaffected by the concentration of the sulphite solution. The latter fact together with the fact that it is not formed in acid solutions shows that the dithionate is produced from SO_3'' ions, and the following equation is given as representing the electrical reaction, $2\text{SO}_3'' + 2\text{OH}' + 2\text{H}' + 2F = \text{S}_2\text{O}_6'' + 2\text{H}_2\text{O}$.

A solution of dithionic acid or of one of its salts is not reduced at the cathode, and undergoes very little oxidation at the anode.

T. E.

Reduction of Nitrates by Certain Plant Extracts and Metals, and the Accelerating Effect of Certain Substances on the Progress of the Reduction. JOSEPH H. KASTLE and ELIAS ELVOVE (*Amer. Chem. J.*, 1904, 31, 606—641).—A freshly prepared aqueous extract of the potato tuber is capable of effecting the reduction of sodium nitrate to nitrite, but this property is destroyed by boiling. The reduction takes place most rapidly at 40—45°. If the quantity of nitrate is increased, the amount of nitrite produced gradually rises to a maximum beyond which a further addition of nitrate retards the reduction. By increasing the amount of potato extract, the reducing action is increased until a maximum is reached beyond which additional quantities of the extract produce no further effect. The reduction is inhibited by mercuric chloride, chloroform, resorcinol, and alkalis, and is considerably weakened by phenol, phenylhydrazine hydrochloride, sodium hypophosphite, quinol, hydroxylamine hydrochloride, benzenesulphinic acid, sodium fluoride, and hydrogen cyanide. On the other hand, certain substances, especially alcohols and aldehydes, cause a considerable acceleration in the reducing action of the potato extract; for example, in the presence of benzyl alcohol or benzaldehyde, the amount of nitrite produced is increased from 25 to 30 times. The reduction in presence of such accelerators is subject to the same conditions as in their absence, and is affected in the same way by changes of temperature and variation in the quantities of nitrate and potato extract employed. The conversion of nitrate into

nitrite by means of potato extract appears to take place most readily in a slightly acid solution but, in presence of an accelerator, acids cause a diminution in the reduction to an extent depending on the quantity and strength of the acid employed.

The aqueous extracts of many other plants were examined, but only the fruit of the egg plant (*Solanum melongena*) and the tubers and sprouts of the potato were found to be capable of effecting the reduction.

The reduction of nitrates by metals was also studied. In the first series of experiments, platinum black was employed, which was prepared by precipitating the metal from its chloride by means of zinc dust, and afterwards washing the precipitate with hydrochloric acid and with water and drying it at the ordinary temperature. The results showed that platinum black prepared in this manner is capable of reducing sodium and potassium nitrates to nitrites, and that the amount of nitrite produced is greatly increased by the presence of such substances as ethyl alcohol, formaldehyde, and formic acid. It was also found that if this platinum black was heated to 100° for half an hour, its activity was slightly increased, whilst if heated to 300° for the same length of time it became much more active. In view of these results, it seemed of interest to study the behaviour of platinum black prepared by other methods, and it was found that none of the specimens so produced possessed the activity of the metal obtained by precipitation with zinc dust, whilst certain of them were totally incapable of effecting the reduction of nitrates. It was discovered that the activity of the first specimen of platinum black was due to the presence of zinc as an impurity.

Pure precipitated silver is quite inactive towards potassium nitrate even in presence of an accelerator, whilst silver-zinc alloy, prepared by immersing zinc in solution of silver nitrate, shows considerable reducing power, especially in the presence of certain other substances, such as formaldehyde.

E. G.

Preparation and Properties of Hypophosphorous Acid.
CHARLES MARIE (*Compt. rend.*, 1904, 138, 1216—1217).—Pure barium hypophosphite, precipitated by alcohol from aqueous solution, dried in the air, dissolved in boiling water, and treated with the theoretical quantity of dilute sulphuric acid, yields a solution of hypophosphorous acid from which the pure acid can be obtained by concentration, first by boiling under the ordinary pressure, and then in a vacuum at 80—90° until there is no further loss in weight. Hypophosphorous acid can also be prepared by treating the dried sodium salt with the theoretical quantity of concentrated sulphuric acid, and after two days extracting the hypophosphorous acid from the sodium sulphate by means of alcohol. Hypophosphorous acid, purified by fractional crystallisation and dried over phosphoric anhydride, melts at 26·5°; its decomposition by heat into orthophosphoric acid and hydrogen phosphide really takes place in two stages: (1) at 130—140°, hydrogen phosphide and phosphorous acid are formed according to the equation $3\text{H}_3\text{PO}_2 = 2\text{H}_3\text{PO}_3 + \text{PH}_3$; (2) at 160—170°, the phosphorous acid is decomposed into phosphoric acid and hydrogen phosphide.

M. A. W.

Apparent Volatilisation of Silicon in Hydrogen. A. DUFOUR (*Compt. rend.*, 1904, 1169—1170. Compare this vol., ii, 398).—The passage of an electric discharge through a Geissler tube filled with silicon hydride immediately causes a deposit of amorphous silicon; if, however, the current is continued for about an hour, the original deposit of silicon gradually disappears and is reformed in the dark space around the cathode. The final deposit is always formed in the dark space, even if other parts of the tube are cooled to 80° ; hence the phenomenon cannot be due to the distillation of the silicon from the hot regions to the colder. The facts can only be explained satisfactorily by supposing the silicon to recombine with the hydrogen present to form silicon hydride, which is decomposed in the dark space by the impact of the corpuscles emitted from the cathode. Arsenic hydride behaves in a similar manner, but in this case the removal of the arsenic can be proved to be due to distillation. S. S.

Synthesis of Silicon Hydride from its Elements. ÉMILE VIGOUROUX (*Compt. rend.*, 1904, 1168).—The author draws attention to the fact that he had already observed the direct formation of silicon hydride from its elements before the publication of a paper by Dufour on that subject (this vol., ii, 398). S. S.

Further Experiments on the Production of Helium from Radium. Sir WILLIAM RAMSAY and FREDERICK SODDY (*Proc. Roy. Soc.*, 1904, 73, 346—358).—The earlier research (*Abstr.*, 1903, ii, 622) has been continued, and details are given of the experiments in which the production of helium from radium has been observed. The authors have examined the gas given off from a solution of radium bromide in 60 days, and formed an estimate of the helium produced by comparing the intensity of its spectrum with that of a known quantity of helium at a known pressure. The experiments show that 1 gram of radium bromide should give in one year 0.0022 mg. of helium.

An attempt has been made to measure also the volume of the emanation in a fine capillary tube, and it is estimated that 1 gram of radium produces 3×10^{-6} cub. mm. of emanation per second. The molecule of the emanation is probably monatomic, and since diffusion experiments indicate a density of about 80, its atomic weight should be about 160. Hence, not more than one atom of emanation can be produced from one atom of radium, and the average life of the radium atom is probably about 1100 years. The total quantity of energy evolved in the change of 1 gram of radium is about 250,000 times the energy evolved in the formation of 1 gram of water.

Comparing their value for the equilibrium quantity of emanation produced by 1 gram of radium with Rutherford's calculated value, the authors consider that there are now direct experimental reasons for believing that (1) only one α -particle is expelled from the atom at each disintegration; (2) the greater part of the energy of disintegration appears in the form of kinetic energy of α -radiation. J. C. P.

Bell Process of Electrolysing Aqueous Solutions of Alkali Chlorides. OTTO STEINER (*Zeit. Elektrochem.*, 1904, 10, 317—331).—The process studied is a technical method of electrolysing solutions of potassium chloride in which the anode is contained in a non-conducting bell, suspended, mouth downwards, in a solution of the salt, the cathode dipping into the solution outside. In these circumstances, the heavy solution of potassium hydroxide formed at the cathode collects at the bottom of the vessel and diffuses slowly up into the bell, where it meets the faintly acid chlorine solution formed at the anode; a neutral layer is thus formed within the bell and below the anode. By constantly feeding fresh solution of potassium chloride into the bell just above the anode, the neutral layer may be maintained stationary at any desired position between the anode and the open mouth of the bell. The author has made a careful study of the conditions necessary to maintain this neutral zone; he finds that the even distribution of the fresh solution over the whole area of the bell is of great importance. This can be attained by dropping the solution on to a horizontal plate of metal wrapped up in glass wool. The greater the concentration of the potassium chloride and the smaller that of the hydroxide, the greater is the distance between the anode and the neutral zone. So long as this distance exceeds 1 cm., graphite anodes are practically unacted on (up to current densities of 0.02 ampere per sq. cm.). Using a saturated solution of potassium chloride, the current efficiency, under these conditions, is from 85 to 94 per cent. so long as the concentration of the hydroxide is not greater than about 130 grams per litre; 3.7 to 4.2 volts are required. T. E.

Velocity of Decomposition of a Mixture of Sodium Nitrite and Ammonium Chloride. E. BERGER (*Bull. Soc. chim.*, 1904, [iii], 31, 662—666. Compare Loew, *Abstr.*, 1891, ii, 16; Angeli and Boeris, *Abstr.*, 1893, ii, 155; Wegscheider, *Abstr.*, 1901, ii, 384; Arndt, *Abstr.*, 1902, ii, 64; and Veley, *Trans.*, 1903, 83, 736).—The author has studied especially the influence of temperature and concentration on the interaction of these two salts in aqueous solution. The decomposition was effected in a Victor Meyer vapour density apparatus, the amount of nitrogen evolved in a selected period of time being used as a measure of the rapidity of the reaction. The results, which are tabulated and illustrated by curves in the original, show that the reaction occurs for all concentrations at temperatures above 0°, that its velocity increases rapidly with rise of temperature, and decreases directly as the concentration diminishes, so long as this does not fall below 50 grams per litre. For more dilute solutions than this, the velocity of reaction diminishes more rapidly, since the salts become largely ionised and so escape the reaction. T. A. H.

Electrolysis of Calcium Chloride. HENRI MOISSAN (*Compt. rend.*, 1904, 138, 1194—1196. Compare this vol., ii, 333).—A reply to Bullier (compare this vol., ii, 403).—The author's experiments differ essentially from those of Bullier in that he uses a mixture of calcium fluoride and chloride, which is liquid at 650°, and readily electrolysed with the formation of a mixture of calcium carbide and calcium, the latter preponderating even in the presence of carbon electrodes; whereas the

mixture of calcium chloride and oxide used by Bullier does not fuse even at 740° , and the electrolysis proceeds irregularly. M. A. W.

Behaviour of Typical Hydrous Chlorides when Heated in Hydrogen Chloride. FRANK A. GOOCH and F. M. McCLENAHAN (*Amer. J. Sci.*, 1904, [iv], 17, 365—376).—An investigation has been made of the influence of hydrogen chloride on the dehydration of the hydrous chlorides of barium, magnesium, and calcium. Two wide glass tubes were heated side by side in a paraffin-bath, each tube being provided with a thermometer. A porcelain boat containing a weighed quantity of the hydrous salt was placed in each tube immediately below the bulb of the thermometer. A current of dry air was passed through one tube and a current of hydrogen chloride through the other. At the close of the experiment, the loss of weight in each case was determined, and the chlorine was estimated in the residue in order to ascertain the proportion of the loss due to water and hydrogen chloride respectively. Tabular statements and diagrams are given which indicate the course of the decomposition of the different salts at various temperatures.

The dehydration of hydrous barium chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, is not affected by hydrogen chloride below 100° , and at this temperature the change is complete. In the case of magnesium chloride, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, hydrogen chloride appears to exert no influence on the removal of the first third of the water, which is eliminated at 100° , but retards the dehydration between 100° and 130° and accelerates it at temperatures above 130° . The hydrolytic dissociation of this salt is not very marked below 200° in either air or hydrogen chloride. The dehydration of aluminium chloride, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, is inhibited by hydrogen chloride below 130° , but above this temperature, as also in air above 100° , both water and hydrogen chloride are evolved simultaneously.

The paper concludes with a discussion of the bearing of these results on the general molecular configuration of hydrous chlorides, and it is shown that a reasonable explanation is afforded by the hypothesis of varying relations in the position of the water in the molecular complex based on the assumption of quadrivalent oxygen as suggested by Cushman (*Abstr.*, 1902, ii, 322). E. G.

Specific Gravities of Lithium Chloride, Bromide, and Iodide. GREGORY P. BAXTER (*Amer. Chem. J.*, 1904, 31, 558—564).—The sp. gr. of carefully purified lithium chloride, bromide, and iodide at $25^{\circ}/4^{\circ}$ have been determined by means of the pycnometer described by Baxter and Hines (this vol., ii, 257), with the following results: fused lithium chloride, 2.068; fused lithium bromide, 3.464; fused lithium iodide, 4.061.

Attention is drawn to a slight error in the calculations which occurred in the recent papers by Baxter and Hines (*loc. cit.*) and Baxter and Lamb (this vol., ii, 257). The corrected values for the sp. gr. are as follows: cadmium chloride, 4.047; cadmium bromide, 5.192; silver bromide, 6.473. The error in the case of zinc chloride is beyond the limit of accuracy of the experiments. E. G.

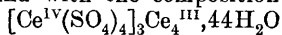
The Characterisation of Lead: Reply to Clemens Winkler. KARL A. HOFMANN (*Ber.*, 1904, 37, 2197—2198).—The author's determination of the equivalent of radioactive lead sulphate (Abstr., 1901, ii, 159) has been objected to by Winckler (this vol., ii, 462) on the ground that the lead sulphate employed was heated only at 400—420°, and may therefore have contained adherent sulphuric acid. Experiments with purified lead nitrate show that excess of sulphuric acid is completely removed from lead sulphate at 355°, and the objection cannot therefore be maintained. C. H. D.

Fractionation of Cerium Earths. HENRI LACOMBE (*Bull. Soc. chim.*, 1904, [iii], 31, 570—573. Compare Auer von Welsbach, Abstr., 1885, 350, and Demarçay, Abstr., 1900, ii, 347).—The author finds that neodymium and praseodymium can be separated from each other and from samarium, and perhaps also from lanthanum, more rapidly and effectually by fractional crystallisation of the double manganese nitrates of the type $2\text{Di}(\text{NO}_3)_2 \cdot 3\text{Mn}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$, than by Demarçay's process. The fractionation is best carried out in nitric acid of sp. gr. 1.3; the volume of the mother liquor should be maintained almost constant, and be very small in comparison with the bulk of crystalline matter separated. The formation of crystals may be initiated by a nucleus of the isomorphous bismuth manganese nitrate. Typical examples of the results of the application of this process to (1) earths rich in neodymium, (2) earths rich in praseodymium, and (3) earths rich in lanthanum, are quoted in the original.

T. A. H.

Salts of the Complex Cerisulphuric Acid with the Elements of the Rare Earths. BOHUSLAV BRAUNER (*Zeit. anorg. Chem.*, 1904, 39, 261—295. Compare Brauner and Picek, this vol., ii, 259; Meyer and Aufrecht, this vol., ii, 175).—An historical survey of researches on cerium sulphates is first given. The author quotes further results with cerium sulphates and describes salts formed from ceric sulphate and lanthanum, praseodymium, and neodymium respectively.

A mixture of yellow ceric sulphate, $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, and red ceroso-ceric hydrogen sulphate, $\text{Ce}_2\text{H}(\text{SO}_4)_4 \cdot 12\text{H}_2\text{O}$, is formed by the action of water and concentrated sulphuric acid on ceric tetroxide. Crystallographic measurements of both salts are given. Ceroso-ceric hydrogen sulphate is also formed synthetically from cerous sulphate and ceric sulphate; the latter must be in excess, and the solution must also contain enough free sulphuric acid to maintain the ceric sulphuric acid in solution. When a mixture of cerous and ceric sulphates in solution is allowed to crystallise in presence of sulphuric acid, just sufficient in amount to prevent the hydrolysis of the ceric salt, an orange-brown compound with the composition



separates. Generally, however, mixtures of normal and acid salts are obtained, the amount of the latter formed depending on the amount of free sulphuric acid present.

In the red ceroso-ceric salt, the trivalent cerium atom may be

replaced by other trivalent atoms. With lanthanum, for example, two salts are obtained. When a solution containing lanthanum sulphate, cerium sulphate, and sulphuric acid just sufficient to prevent the hydrolysis of the ceric salt is allowed to crystallise, the orange-yellow salt of the composition $[\text{Ce}^{\text{IV}}(\text{SO}_4)_4]_3\text{La}_4^{\text{III}}, 44\text{H}_2\text{O}$ separates. On the other hand, when the mixture contains an excess both of ceric sulphate and sulphuric acid, the salt $\text{Ce}^{\text{IV}}(\text{SO}_4)_4\text{La}^{\text{III}}\text{H}, 12\text{H}_2\text{O}$ separates. The salts $\text{Ce}(\text{SO}_4)_4\text{PrH}, 12\text{H}_2\text{O}$ and $\text{Ce}(\text{SO}_4)_4\text{NdH}, 12\text{H}_2\text{O}$ were formed in an analogous manner.

Cerosceric hydrogen sulphate and the salts formed by the replacement of the trivalent cerium in it by lanthanum, praseodymium, and neodymium respectively separate in hexagonal crystals; they are isomorphous and form mixed crystals. A. McK.

Preparation of Samarium Oxide and the Atomic Weight of Samarium. GEORGES URBAIN and HENRI LACOMBE (*Compt. rend.*, 1904, 1166—1168. Compare Abstr., 1904, ii, 37, 173, 340).—Samarium oxide was prepared by a method which has been described in a previous communication. The purity of the product is proved by the fact that the atomic weight of the metal does not vary greatly in material obtained from different sources. The atomic weight of samarium was determined in three ways: by the conversion of (1) the hydrated sulphate, $\text{Sa}_2(\text{SO}_4)_8 \cdot 8\text{H}_2\text{O}$, into the anhydrous salt, $\text{Sa}_2(\text{SO}_4)_3$; (2) of the anhydrous sulphate into the oxide, Sa_2O_3 ; (3) of the hydrated sulphate into the oxide. The mean of three experiments with each of these methods gave 153.340, 150.346, and 150.346 respectively ($\text{O}=16$). The atomic weight may therefore be taken as 150.34. S. S.

Action of Certain Solutions on Aluminium and Zinc. WATSON SMITH (*J. Soc. Chem. Ind.*, 1904, 23, 475—477).—The action of solutions of phosphoric acid, sulphuric acid, acetic acid, nitric acid, ammonia, sodium carbonate, ammonium phosphate, ammonium arsenate, sodium chlorate, sodium nitrate, and potassium nitrate on aluminium and zinc respectively has been examined, as also has been the action of cold and hot water on these metals. A. McK.

Aluminium-Tin Alloys. E. S. SHEPHERD (*J. Physical Chem.*, 1904, 8, 233—247).—Although various workers have investigated these alloys, their results left in doubt the existence of definite compounds, such as AlSn and Al_4Sn , whilst other points recorded required confirmation. The author therefore determined the freezing points of alloys of from 10 to 50 per cent. aluminium, taking many precautions to ensure accuracy; the greatest difference obtained for the freezing point of any alloy is only 4 degrees. The curve obtained is perfectly continuous and does not indicate the existence of any definite compound. Previous observers had found either a minimum at about 20 per cent. aluminium or a constant temperature between about 17 and 25 per cent., but neither of these observations was confirmed. The flatness of the curve might be expected to indicate an unstable region of two liquid layers below the freezing point curve,

but experiments showed that this does not exist. The densities of various alloys were determined and the values and curves are given. Photographs are also given of the etched surface of different alloys. These help to confirm the author's view that the tin exists in the form of a solid solution up to the concentration of about 20 per cent.

L. M. J.

A Property of Tin-Aluminium Alloys. HECTOR PÉCHEUX (*Compt. rend.*, 1904, 1170—1171).—Electrolytic gas is evolved if a recently filed rod of tin-aluminium alloy is immersed in cold distilled water. The evolution of gas may be prolonged by increasing the filing of the metal. The phenomenon seems to be due to the juxtaposition of the molecules of each metal. The specific heats of aluminium and tin are widely different, hence after the action of the file the molecules of each metal will be at different temperatures and a series of thermo-electric couples will be established when the alloy is immersed in water.

S. S.

Constitution of Ultramarine. PAUL ROHLAND (*Zeit. angew. Chem.*, 1904, 17, 609—616).—Mainly historical. Ultramarine, when mixed with Portland cement, undergoes hydration and combines with the free calcium hydroxide in the cement. It also undergoes hydration in the absence of Portland cement, and the rate of this hydration is influenced by positive catalysers, such as aluminium chloride and sodium carbonate. Sodium chloride in dilute solution acts as a positive catalyser in the case of ultramarine, whilst it has no action under the same conditions with Portland cement; in more concentrated solution, it acts as a retarder with Portland cement. The hydration of ultramarine is a feebly exothermic reaction. The hydration and hardening of ultramarine are doubtless aided by the formation from it by heat of a dilute solid solution of sodium oxide with the silicious constituents.

A. McK.

Indium. CARL RENZ (*Ber.*, 1904, 37, 2110—2112).—Dennis and Geer's recent method for the purification of indium by means of tripyridine indium chloride (this vol., ii, 342) had been previously described by the author (*Abstr.*, 1903, i, 774; ii, 548 and 729).

Indium oxide, when heated to a white heat in an iridium dish, sublimes without previously melting. The greyish-white powder formed on cooling contains abundant glistening crystals. Two modifications of indium oxide are to be distinguished—a yellow, amorphous form, soluble in acids, and a crystalline form insoluble in acids. Metallic indium combines with selenium and tellurium, forming black masses with a metallic lustre.

E. F. A.

Soluble Colloidal Form of Ferric and of Other Phosphates. WILLIAM J. SELL (*Proc. Camb. Phil. Soc.*, 1904, 12, 388—390).—In presence of ammonia, diammonium hydrogen phosphate dissolves a considerable quantity of ferric phosphate to a brownish-red solution. If the solution is dialysed until all electrolytes are removed, it may be shown to contain ferric phosphate, which is slightly basic, owing to a

little ferric hydroxide. The colloidal solution of ferric phosphate is tasteless and without action on litmus. Addition of alkali chlorides and most other salts induces gelatinisation. The very small value of the conductivity points to there being no free iron ions in the solution, and this is confirmed by the failure of potassium thiocyanate and ferrocyanide to give any colour reaction; these reagents cause gelatinisation only. On the other hand, hydrogen sulphide and ammonium sulphide both give black precipitates.

Aluminium and chromium phosphates also give colloidal solutions, which, although weaker, behave similarly to that of ferric phosphate.

J. C. P.

Preparation of Nickel Carbonyl and Metallic Nickel. Sir JAMES DEWAR (D.R.-P. 149959).—The formation of nickel carbonyl from nickel and carbon monoxide, which takes place at 50° under the ordinary pressure, may be advantageously carried out under a pressure of 2–100 atmospheres, in which case the temperature may be raised even to 250° without causing decomposition. The reaction is in this way greatly accelerated. Moreover, the condensation of the nickel carbonyl is best performed under pressure, so that the excess of carbon monoxide may be led back over the nickel under the same pressure. A suitable apparatus is described and figured.

C. H. D.

Action of Alkali Nitrites on Nickel Salts. I. C. REICHARD (*Chem. Zeit.*, 1904, 28, 479–480).—Double nickel nitrites with the alkaline earth metals are capable of being formed even in the absence of the hydroxides of these metals. When barium nitrate is added to a mixture of nickel nitrate and potassium nitrite, the double salt is gradually precipitated; there is no precipitation, however, when acetic acid has first been added to the nickel nitrate and potassium nitrite. Strontium nitrate has the same effect as barium nitrate. Calcium nickel potassium nitrite was prepared. The action of magnesium, zinc, and cadmium salts towards nickel salts in the presence of alkaline nitrites was also studied. Sodium nitrite was also substituted for potassium nitrite in the formation of nickel double nitrites.

A. McK.

Amount of Chlorine which can be Precipitated by Silver Salts from the Green Hydrate of Chromium Chloride or Bromide. RUDOLF F. WEINLAND and A. KOCH (*Zeit. anorg. Chem.*, 1904, 39, 296–329. Compare Werner and Gubser, *Abstr.*, 1901, ii, 453; Wyruboff, *Abstr.*, 1902, ii, 565).—The authors have examined the behaviour of the hydrate of chromium chloride, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, towards silver salts, and find that the amount of chlorine precipitated depends on the nature and the quantity of the particular silver salt used and especially on the nature and the quantity of the particular acid added. Of the silver salts examined, all, without the addition of acids, precipitate at least two-thirds of the chlorine, some of them precipitate more, and some precipitate the chlorine entirely. When the precipitations were conducted in alcoholic solutions, all the chlorine was precipitated without the addition of acid; when nitric acid was added, the amount of the chlorine precipitated diminished. With the green hydrate of chromium bromide, the various silver salts examined

precipitated the bromine entirely without the addition of acid; by the addition of certain acids, however, the amount of the precipitated bromine could be diminished to two-thirds of the total. The silver salts of weak acids, such as acetic, lactic, and nitrous acids, and silver sulphate precipitate the chlorine completely from solutions of the hydrate of chromium chloride, whilst the silver salts of strong acids do not. Many figures are quoted to show the percentage of chlorine precipitated under such different conditions as by silver nitrate and nitric acid, silver sulphate and sulphuric acid, silver chlorate and chloric acid, silver perchlorate and perchloric acid, silver permanganate and permanganic acid, silver lactate and lactic acid, silver acetate and acetic acid.

Solutions of the double chloride, $\text{CrCl}_3 \cdot 2\text{CsCl} \cdot 4\text{H}_2\text{O}$, were also studied. A. McK.

Preparation of Crystallised Zirconium in the Electric Furnace. EDGAR WEDEKIND (*Zeit. Elektrochem.*, 1904, 10, 331—335).—Potassium zirconium fluoride is fused with excess of aluminium in an electric arc furnace. The product is extracted with hydrochloric acid and potassium hydroxide solution in order to remove excess of aluminium. Crystalline plates, having the appearance of antimony, are left, which contain about 34 per cent. of aluminium, corresponding nearly with the formula ZrAl_2 . The substance is dissolved by hydrofluoric acid or by fused alkalis; no other usual substance acts on it with the exception of hot aqua regia, which dissolves it slowly. It only undergoes superficial oxidation when heated in a blowpipe flame. It conducts electricity, and may be fused by compressing it in a quartz tube and passing a current of electricity through it (using platinum terminals). The fused substance contains less aluminium than the original material, its composition being approximately Zr_3Al_4 . The substance ZrAl_2 apparently crystallises in the regular system, and the author considers it to be a real compound and not an alloy.

An experiment in which magnesium was used to reduce potassium zirconium fluoride gave a product from which all the magnesium could be removed, leaving a substance containing 94.1 per cent. of zirconium. It may be possible in this way to obtain pure crystalline zirconium.

Electrolysis of the fused double salt gave only amorphous zirconium. T. E.

Decomposition of Antimony Hydride. ALFRED STOCK and OSKAR GUTTMANN (*Ber.*, 1904, 37, 1957—1960. Compare this vol., ii, 413).—A reply to Bodenstein (this vol., ii, 246). W. A. D.

The Melting Point of Gold. DANIEL BERTHELOT (*Compt. rend.*, 1904, 1153—1155).—The most accurate determinations of the melting point of gold have been made by the author (*Abstr.*, 1898, ii, 341), by Jacquerod and Perrot (*Compt. rend.*, 1904, 138, 864), and by Holborn and Day (*Abstr.*, 1901, ii, 85). The numbers obtained by these investigators are corrected, when they become 1065.6° (Berthelot), 1067.4° (Jacquerod and Perrot), and 1064.3° (Holborn and Day).

S. S.

Solubility of Gold in Certain Oxidising Agents. VICTOR LENHER (*J. Amer. Chem. Soc.*, 1904, 26, 550—554).—Gold is dissolved by a solution of crystalline telluric acid in sulphuric or phosphoric acid. Since, during the solution of gold either by telluric or selenic acid, the acids are converted into dioxides and oxygen is evolved, it appeared probable to the author that the solvent action in those cases is due to the production of oxygen in the reaction. The substances employed by the author were halogen-free; only those substances which give oxygen in presence of acids act on gold. A mixture of manganese dioxide and concentrated sulphuric acid readily dissolves gold when heated with it for a few minutes. Solution also takes place slowly at low temperatures. The higher oxides of manganese behave in a similar manner. Gold is also dissolved when heated with solid potassium permanganate and sulphuric acid (or phosphoric acid). Lead dioxide, lead sesquioxide, and red lead, when heated with sulphuric acid, also dissolve gold; with the higher oxides of lead, phosphoric acid may be substituted for sulphuric acid. Chromium trioxide, chromium tetroxide, and nickelic oxide behave similarly. Gold is soluble when heated with a mixture of nitric and sulphuric acids. The action of oxygen gas on gold leaf suspended in hot sulphuric acid was also tried, but neither oxygen nor ozone caused any of the metal to dissolve. When oxygen is formed at the anode during electrolysis of sulphuric acid, gold is dissolved quickly when the acid is concentrated; when the acid is dilute, the anode is coated with an incrustation of the oxide. Similar results were obtained when phosphoric acid is substituted for sulphuric acid, or when the hydrogen sulphates of potassium or sodium are employed. In the case of an alkaline electrolyte, some of the gold passes through the solution, probably from the formation of an alkali aurate; with neutral salt solutions, very little, if any, of the gold passes through the electrolyte, the anode being converted into the oxide, Au_2O_3 . In these electrolytic experiments, the current used was 0.3—0.5 ampere at a pressure of 5 volts, the anode being a sheet of gold and the cathode a platinum crucible. A. MCK.

Ruthenium. V. Ruthenium Chlorides. JAMES L. HOWE (*J. Amer. Chem. Soc.*, 1904, 26, 543—549. Compare Abstr., 1902, ii, 86).—Potassium aquochlororuthenate, $\text{K}_2\text{Ru}(\text{OH}_2)\text{Cl}_5$, prepared by boiling a slightly acidified (with hydrochloric acid) solution of potassium chlororuthenite with alcohol, or by boiling a solution of the hydrated sesquioxide in hydrochloric acid with alcohol, crystallises in orthorhombic octahedra; on boiling, its solution becomes greenish-brown; its characteristic reaction is the immediate darkening of its solution on addition of bromine or chlorine water. The salt is stable up to 140° ; between 140° and 180° , it loses water, passing into potassium chlororuthenite, K_2RuCl_5 .

Aquochlororuthenates of the type $\text{X}_2\text{Ru}(\text{OH}_2)\text{Cl}_5$ are isomeric with chlororuthenites, which are thus represented: $\text{X}_2\text{RuCl}_5 \cdot \text{H}_2\text{O}$. Crystals of the dehydrated potassium aquochlororuthenate preserve the form of the aquo-salt; their solution differs from that of potassium chlororuthenite. Aqueous solutions of the chlororuthenite and the aquo-

chlororuthenate undergo a similar decomposition in water, accompanied by an increase in the conductivity, but the increase is much slower in the case of the aquo-salt. Whilst the initial value for the conductivity is the same for the two salts, the final value for the aquo-salt is much less than that for the chlororuthenite.

Ammonium aquochlororuthenate, $(\text{NH}_4)_2\text{Ru}(\text{OH}_2)\text{Cl}_5$, prepared by boiling ammonium chlororuthenite with dilute acidified alcohol, crystallises with difficulty; when chlorine is passed into its concentrated aqueous solution, *ammonium chlororuthenate*, $(\text{NH}_4)_2\text{RuCl}_6$, is produced. *Potassium chlororuthenate*, K_2RuCl_6 , prepared by the action of chlorine on a concentrated acid solution of potassium aquochlororuthenate, forms minute, black octahedra, easily soluble in, and rapidly decomposed by, boiling water to form a pale purplish-brown solution. *Cæsium chlororuthenate*, Cs_2RuCl_6 , is prepared in an analogous manner.

A. McK.

Mineralogical Chemistry.

Artificial Production of Crystallised Domeykite, &c. GEORGE A. KOENIG (*Proc. Amer. Phil. Soc.*, 1903, 42, 219—237; *Zeit. Kryst. Min.*, 1904, 38, 529—554).—A glass tube containing arsenic at one end and metallic copper (filings, turnings, or wire) in the middle was heated to dull redness (about 600°) by means of an electric current passing through a platinum wire wound around the tube. As the arsenic sublimes over the heated copper, brilliant crystals of copper arsenide, Cu_3As (domeykite), are seen to grow out from the surface of the copper, the growth taking place in such a manner as to suggest that there must be a free movement of the copper molecules.

Using, in place of copper, an alloy of copper, nickel, and cobalt, crystals of $(\text{Cu},\text{Ni},\text{Co})_3\text{As}$ (mohawkite, Abstr., 1901, ii, 109) were obtained; with an alloy of copper and silver, crystals of $(\text{Cu},\text{Ag})_3\text{As}$ (argento-domeykite) and of $(\text{Cu},\text{Ag})_6\text{As}$ (argento-algodonite); and with an alloy of copper and antimony, crystals of $\text{Cu}_3(\text{As},\text{Sb})$ (stibio-domeykite; Abstr., 1901, ii, 109). When arsenic vapours are passed over zinc, lead, or nickel, there is also some action, but no crystals were formed.

A crystallographic description by FRED. EUGENE WRIGHT is given of the artificial crystals of domeykite, argento-domeykite, and mohawkite, all of which are holohedral hexagonal. Artificial crystals of domeykite have previously been described as orthorhombic (Abstr., 1903, ii, 301).
L. J. S.

Artificial Production of Brushite and Monetite. AUGUST B. DE SCHULTEN (*Bull. Soc. franç. Min.*, 1903, 26, 11—17).—Crystals of brushite ($\text{H}_2\text{CaP}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$) suitable for goniometric measurement were obtained by dissolving precipitated hydrogen calcium phosphate in

acetic acid (25 per cent.) and allowing the solution to slowly evaporate at the ordinary temperature. At temperatures above 50° , the solution deposits crystals of monetite (HCaPO_4). Attempts to produce meta-brushite ($\text{HCaPO}_4 \cdot 1\frac{1}{2}\text{H}_2\text{O}$) were without success, and reasons are given for considering this to be identical with brushite. Crystallographic descriptions are given.

L. J. S.

Artificial Production of Newberyite. AUGUST B. DE SCHULTEN (*Bull. Soc. franç. Min.*, 1903, 26, 24—29).—Crystals of the salt $\text{HMgPO}_4 \cdot 7\text{H}_2\text{O}$ are obtained by allowing a solution of phosphoric acid to act on magnesium carbonate, and when these remain for some time in contact with the liquid they are converted into crystals of newberyite ($\text{HMgPO}_4 \cdot 3\text{H}_2\text{O}$). Debray's salt, $\text{HMgPO}_4 \cdot 4\frac{1}{2}\text{H}_2\text{O}$, consists of a mixture of these. Crystals of newberyite, suitable for goniometric measurement and of varying habits, were obtained by the following methods: heating a solution of magnesium carbonate in phosphoric acid in a sealed tube at 150° ; evaporating on the water-bath an acetic acid solution of hydrogen magnesium phosphate; and by the method employed for the production of crystallised monetite (*Abstr.*, 1902, ii, 89).

L. J. S.

Artificial Production of Pharmacolite and Haidingerite. AUGUST B. DE SCHULTEN (*Bull. Soc. franç. Min.*, 1903, 26, 18—24).—Crystals of pharmacolite ($\text{HCaAsO}_4 \cdot 2\text{H}_2\text{O}$) are deposited from a clear solution containing calcium chloride, hydrochloric acid, and hydrogen sodium arsenate. From more concentrated solutions, crystals of both pharmacolite and haidingerite ($\text{HCaAsO}_4 \cdot \text{H}_2\text{O}$) are deposited. Measurable crystals of haidingerite were obtained by the method previously employed for preparing crystallised monetite (*Abstr.*, 1902, ii, 89).

L. J. S.

Formation of Oceanic Salt Deposits. XXXVI. Combinations of Minerals from 25° to 83° . JACOBUS H. VAN'T HOFF and WILHELM MEYERHOFFER (*Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 659—670).—A general review of all previous results. So far as the changes in the mutually possible combinations are concerned, the above temperature range may be divided into three intervals. The first interval, 25 — 37° , is marked by the disappearance of schoenite, reichardtite, and magnesium sulphate hexahydrate. The second interval, 37 — 55° , covers the appearance of langbeinite, loeweite, vanthoffite; whilst in the third interval, 55 — 83° , blödite, leonite, and kainite successively disappear from the equilibrium diagrams.

The various changes and transformations that take place in presence of sodium chloride between 25° and 83° are fully given in the following summary:

I. Changes involving the splitting off of water.

A. Transformation of schoenite into leonite.

- (1) In presence of glaserite and potassium chloride (25.5°).
- (2) In presence of glaserite and blödite (26°).

B. Transformation of reichardtite into magnesium sulphate hexahydrate.

- (1) In presence of leonite and kainite (27°).
- (2) In presence of leonite and blödite (27·5°).
- (3) In presence of blödite (31°).

C. Transformation of hexahydrate into kieserite.

- (1) In presence of leonite and kainite (31·5°).
- (2) In presence of leonite and blödite (32°).
- (3) In presence of blödite (35·5°).

D. Transformation of blödite into loeweite.

- (1) In presence of langbeinite and kieserite (43°).
- (2) In presence of langbeinite and leonite (47°).
- (3) In presence of kieserite (49°).
- (4) In presence of glaserite and leonite (56·5°).
- (5) In presence of glaserite and vanthoffite (59·5°).
- (6) In presence of vanthoffite (60°).

II. Changes involving the formation of double salts.

A. Transformation of leonite and kieserite into langbeinite.

- (1) In presence of kainite (37°).
- (2) In presence of blödite (37·5°).

B. Transformation of blödite and thenardite into vanthoffite.

- (1) In presence of glaserite (46°).
- (2) Alone (48·5°).

C. Transformation of leonite into glaserite and langbeinite.

- (1) In presence of potassium chloride (60·5°).
- (2) In presence of loeweite (61·5°).

D. Transformation of kainite into kieserite and potassium chloride.

- (1) In presence of carnallite (72°).
- (2) In presence of langbeinite (83°).

III. Transformation at 55° of leonite and kainite into langbeinite and potassium chloride.

For the purpose of applying these results, the following table will be found useful. It shows the temperature limits within which the combination indicated may occur. A + sign means that the combination is possible over the whole range, 25—83°; a - sign or blank means that the combination is not possible within that temperature interval.

| | Langb. | Vanth. | MgSO ₄ 6aq. | Carn. | Leon. | Glas. | |
|------------------------|-----------|-----------|------------------------|-----------|-----------|-----------|------------------------|
| Then. ... | — | above 46° | — | — | — | + | Then. |
| MgSO ₄ 7aq. | — | — | up to 31° | — | up to 28° | — | MgSO ₄ 7aq. |
| Schön. ... | — | — | — | — | up to 26 | up to 26° | Schön. |
| Loew. ... | above 43° | above 60 | — | — | 47—62 | above 57 | Loew. |
| Blöd. ... | 38—47 | 46—60 | 28—36 | — | up to 57 | up to 60 | Blöd. |
| Kies. ... | above 37 | — | up to 36 | + | 32—38 | — | Kies. |
| Kain. ... | 37—83 | — | up to 32 | up to 72° | up to 55 | — | Kain. |
| KCl ... | above 55 | — | — | + | up to 61 | + | KCl |
| Glas. ... | above 61 | about 46 | — | — | 26—62 | Glas. | |
| Leon. ... | 37—62 | — | 27—32 | — | Leon. | | |
| | Langb. | Vanth. | MgSO ₄ 6aq. | Carn. | | | |

| | KCl. | Kain. | Kies. | Blöd. | |
|------------------------|------|-----------|-----------|-----------|------------------------|
| Then. ... | — | — | — | up to 49° | Then. |
| MgSO ₄ 7aq. | — | up to 27° | — | up to 31 | MgSO ₄ 7aq. |
| Schön. ... up to 26° | — | — | — | up to 26 | Schön. |
| Loew. .. | — | — | above 43° | 43—60 | Loew. |
| Blöd. ... | — | — | 32—49 | Blöd. | |
| Kies. ... above 72 | — | up to 83 | Kies. | | |
| Kain. .. up to 83 | KCl. | Kain. | | | |

J. C. P.

Barytes from dep. Lozère. GUÉDRAS (*Compt. rend.*, 1904, 138, 1440).—The occurrence of veins of barytes at Altier (with ores of copper and tin) and at Villefort (with lead ore) is noted. L. J. S.

Soretite, a new Variety of Amphibole. LOUIS DUPARC and FRANCIS PEARCE (*Bull. Soc. franç. Min.*, 1903, 26, 126—135).—This variety of amphibole forms, with anorthite and accessory apatite and magnetite, veins of anorthite-diorite (anal. I) in the dunite and koswite of the Koswinsky Kamen in the northern Urals. Its reference to a new variety is based on the optical characters [$\alpha = 1.6856$, $\beta = 1.6765$, $\gamma = 1.6628$; $2V = 82^\circ 30'$; optically negative; extinction on (010), 17° ; pleochroism, α dark green, β green, γ pale greenish-yellow], which vary slightly in different specimens, and on the chemical composition (anal. II); sp. gr. 3.223:

| | SiO ₂ . | TiO ₂ . | Al ₂ O ₃ . | Cr ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | MnO. |
|-----|--------------------|--------------------|----------------------------------|----------------------------------|----------------------------------|-------|-------|
| I. | 40.30 | — | 17.63 | 0.34 | 6.35 | 10.28 | trace |
| II. | 4.52 | 1.71 | 10.99 | — | 9.64 | 9.83 | trace |

| | CaO. | MgO. | Na ₂ O. | K ₂ O. | Loss on ignition. | Total. |
|-----|-------|-------|--------------------|-------------------|-------------------|--------|
| I. | 13.85 | 8.23 | 2.48 | 0.26 | 0.92 | 100.64 |
| II. | 12.33 | 11.82 | 2.38 | 0.68 | 0.50 | 100.40 |

L. J. S.

Meteoric Irons of Ranchito [Bacubirito] and Casas Grandes. EMIL W. COHEN (*Mitth. naturw. Ver. Neu-Vorpommern u. Rügen*, 1904, 35 (1903), 3—13).—Ranchito, near Bacubirito, Sinaloa, Mexico (compare Abstr., 1902, ii, 669).—This consists mainly of fine grained plessite; the structure is octahedral with very fine lamellæ. Sp. gr. 7.589; analysis gave the results under I.

Casas Grandes, El Paso del Norte, Chihuahua, Mexico (compare Abstr., 1902, ii, 670).—This is an octahedrite with lamellæ of medium width, and is rich in tænite. Sp. gr. 7.885; analysis II.

| | Fe. | Ni. | Co. | Cu. | Cr. | C. | P. | S. | Cl. | Chromite. | Total. |
|-----|-------|------|------|------|------|------|------|------|------|-----------|--------|
| I. | 89.54 | 9.40 | 0.98 | 0.02 | 0.02 | 0.01 | 0.12 | 0.02 | 0.02 | 0.01 | 100.14 |
| II. | 92.66 | 7.26 | 0.94 | — | 0.03 | — | 0.18 | 0.02 | — | 0.03 | 101.12 |

L. J. S.

Physiological Chemistry.

The Palæochemistry of the Ocean in Relation to Animal and Vegetable Protoplasm. ARCHIBALD B. MACALLUM (*Trans. Canadian Institute*, 1903—1904).—The composition of the ocean represents the result of (1) the action of water on the land in past ages, and (2) the chemical and other agencies modifying the power of sea water to retain mineral constituents in solution. In river water, the calcium is always more, and the potassium less abundant than sodium, whilst the magnesium approximates to the latter in amount. In the sea, the sodium is much more abundant than the other three elements. This is due to fixation of the calcium in limestone deposits, to the fixation of potassium in animal and vegetable organisms, and subsequently in glauconite and other potassium-holding deposits. The magnesium added by river water exceeds that removed from the sea, and in consequence is increasing in the ocean, although not so rapidly as the sodium. In the early geological periods, the proportions of these elements must have been different from what they are now, and must have approximated to the proportion now found in river water. It is assumed that this early condition lasted until the appearance of life, and the earliest unicellular organisms acquired a fixed relation of the given elements during what was doubtless a long period. When, later, land organisms appeared and soils were formed, the removal of potassium to the sea was diminished. This, combined with the fixation of potassium and of calcium in the sea already mentioned, has kept these elements fairly constant since that remote period. But in the transition stage, unicellular organisms became multicellular, and developed circulatory systems, the fluid in which was at first modified sea water. In the blood-plasma of vertebrates, sodium, potassium, and calcium are relatively strikingly like those which now obtain in sea water; the magnesium only is present in smaller proportion. This is due to heredity and reproduces the conditions of sea water at the date when a circulatory system first appeared. If it were possible to determine the proportion of the four elements in protoplasm, apart from that in inert and adventitious structures formed by living cells, it is surmised that their proportion would be that of sea water before the development of the circulation.

W. D. H.

Effects of Breathing Rarefied Air. J. TISSOT (*Compt. rend.*, 1904, 138, 1454—1456).—The effect on man of breathing air containing 11 per cent. of oxygen, that is, equivalent to air at an altitude of 5000 metres, as measured by the respiratory exchange, is negligible.

W. D. H.

The Eggs of *Acanthias vulgaris*. EMIL ZDAREK (*Zeit. physiol. Chem.*, 1904, 41, 524—529).—These eggs contain 47 per cent. of dry material, containing inorganic substances, especially phosphates, and probably free metaphosphoric acid. Protamine is absent; fat and

cholesterol are present ; the fat includes phosphorised fat. The main constituent is proteid, of which elementary analyses are given : on decomposition, the principal substance obtained is leucine ; glycine is also found, and small quantities of arginine and lysine. W. D. H.

Albumin of Fishes' Eggs, compared with that in the Sperm in the Same Species. LOUIS HUGOUNENQ (*Compt. rend.*, 1904, 138, 1062—1064).—Herring's eggs contain 6.5 lecithin, 10.3 fat, 2.3 keratin, and 81.5 proteid per cent. The latter presents the chief characters of vitellin: analysis gave C, 53.68; H, 7.38; N, 14.64; S, 0.40; O, 23.90 per cent. On decomposition, it yields leucine, tyrosine, other amino-acids, and hexone bases. In containing a proteid of this character, the egg contrasts with the sperm, in which the principal proteid matter is nucleo-proteid and protamine. W. D. H.

Albumin of Frog's Eggs. J. GALIMARD (*Compt. rend.*, 1904, 138, 1354—1355).—The proteid obtained from frog's eggs is termed *ranovin*. It gives the usual proteid reactions and appears to be allied to vitellin. In its percentage of nitrogen and the proportion of amino-acids obtained from it, it differs somewhat from Hugounenq's clupeovin obtained from herring's eggs (Compare preceding abstract). W. D. H.

Diffusible Alkali and Alkali-tension of the Blood in Disease. KURT BRANDENBURG (*Chem. Centr.*, 1904, i, 1369—1370; from *Zeit. klin. Med.*, 45, 157—199).—Numerous numerical data on the alkalinity of the blood in various conditions. It has but little influence in the molecular concentration of the blood. W. D. H.

Blood Coagulation. LEO LOEB (*Chem. Centr.*, 1904, i, 1281—1282; from *Virchow's Archiv*, 176, 10—47. Compare Abstr., 1904, ii, 353).—Agglutination and fibrin formation are two separate phenomena. Heating the blood of the guinea-pig to 50° does not influence the former, but prevents the latter. The action of tissues in accelerating the coagulation of blood-plasma, is regarded as specific, and not due to lymph. Numerous bacteria, especially *Staphylococcus pyogenes aureus*, hasten clotting. W. D. H.

Agglutination and Hæmolysis by Chemical Precipitates. O. GENGOU (*Compt. rend.*, 1904, 138, 926—928).—A preliminary notice showing that certain precipitates, such as calcium fluoride and barium sulphate, agglutinate and hæmolyse the red corpuscles of rabbit, ox, and fowl. They absorb fibrin ferment, and in certain cases fibrinogen also. W. D. H.

Agglutination of Red Corpuscles by Colloidal Ferric Hydroxide, Sodium Chloride, and Different Serums. MADAME GIRARD-MANGIN and VICTOR HENRI (*Compt. rend.*, 1904, 138, 1461—1463).—Red corpuscles of dog, horse, and rabbit, obtained by centrifugalising, and suspended in an isotonic solution of salt or sugar, are agglutinated by a small amount of colloidal ferric hydroxide; the addition of serum, even after being heated at 60°, prevents this, but a serum

which itself causes agglutination is not made more active by ferric hydroxide. Differences in detail are noted between different animals, and also between the corpuscles when in sugar or salt solutions. Starch prevents agglutination by ferric hydroxide, by normal serum, and by excess of sodium chloride, but not that produced by a specific serum.

W. D. H.

Influence of the Stromata and Liquid of Laked Corpuscles on the Production of Hæmolysins and Agglutinins. GEORGE N. STEWART (*Amer. J. Physiol.*, 1904, 11, 250—281).—The stromata and hæmoglobin-containing fluid of coloured corpuscles, laked by various agents, when injected into animals of another species, causes the production of specific hæmolysins and agglutinins. In general, the hæmolytic effect is most marked after the injection of the stromata, and the hæmolytic effect after the injection of the liquid. But the results do not warrant the conclusion that in the intact corpuscle the substance which causes the production of agglutinin is all in the stroma, and the substance which produces the hæmolysin is all in the cellular contents.

Corpuscles fully fixed by formaldehyde cause on injection the production of specific agglutinins, and to a smaller extent of specific hæmolysins; they are also capable of being agglutinated by specific sera.

W. D. H.

Influence of Hæmorrhage on Metabolism. PHILIP B. HAWK and WILLIAM J. GIES (*Amer. J. Physiol.*, 1904, 11, 171—236. Compare this vol., ii, 184).—A full account of experiments, a preliminary notice of which has already appeared.

W. D. H.

Velocity of Pepsin Secretion in the Dog. REGINALD O. HERZOG (*Zeit. physiol. Chem.*, 1904, 41, 425—436).—A mathematical formula relating to the velocity of pepsin secretion is given, which holds for feeding both on meat and bread. In milk feeding, the secretion is more rapid, and the intense stimulation of the mucous membrane may be there due to the fluidity of the food. If the meat is prevented from reaching the stomach by a previous œsophagotomy, irregular figures are obtained, the rapidity of secretion being then probably influenced by nervous stimuli.

W. D. H.

Digestibility of Connective Tissue Mucoids in Pepsin-Hydrochloric Acid. E. R. POSNER and WILLIAM J. GIES (*Amer. J. Physiol.*, 1904, 11, 330—350).—The mucoids of connective tissue are digestible, although very slowly, in pepsin-hydrochloric acid. A considerable amount (at least 10 per cent.) of undigested residue is always left. The soluble products (muco-albuminate, muco-proteoses, mucopeptones) resemble ordinary peptic products. The indigestible matter consists of resistant compounds of proteid and glucothionic acid; the mucoproteoses contain also a good deal of glucothionic acid, although whether this is an accidental admixture is not settled. The glucothionic acid is similar to chondroitin-sulphuric acid. The peptones do not contain it. The mucoids of connective tissue are readily digested by trypsin in alkaline solution. Leucine, tyrosine, and tryptophan are produced from them in abundance.

W. D. H.

Proteid in Nutriment for Human Beings. HENRI LABBÉ and MORCHOISNE (*Compt. rend.*, 1904, 138, 1365—1367).—In an experiment performed on one of the authors for 38 days, the amount of nitrogen in the food was decreased to as little as 2 or 3 grams daily. The subject of the experiment is stated to have remained in perfect health, but the figures given show a slight diminution of body-weight, and on the days when least proteid was taken, an output of nitrogen greater than the intake. W. D. H.

Proteid Synthesis in the Animal Body. OTTO LOEWI (*Zeit. Biol.*, 1904, 46, 110—112). ERNST J. LESSER (*ibid.*, 113—117).—Polemical. The first-named author believes in proteid synthesis from the products of proteolysis, and criticises the results of the second author, who does not. The second paper is a reply to the first. W. D. H.

Quantitative Analysis of Brain and Spinal Cord. WALDEMAR KOCH (*Amer. J. Physiol.*, 1904, 11, 303—329).—The present paper relates mainly to methods of analysis. The following table gives the principal results so far obtained :

| | White matter of corpus callosum. | Cortex of prefrontal region. | Grey matter free from white. |
|-----------------------------|--|------------------------------------|------------------------------------|
| Proteids..... | 10.0 | 27.7 | 21.7 |
| Nucleo-proteids | 11.5 | 16.6 | 9.6 |
| Neuro-keratin | 8.4 | 2.2 | |
| Extractives | 4.7 | 8.8 | 5.9 |
| Lecithins | 16.2 | 17.4 | 7.7 |
| Kephalin and myelin | 10.9 | 4.1 | |
| Phrenosin and kersasin..... | 14.3 | 8.6 | |
| Cholesterol | 15.2 | 3.9 | |
| Sulphur compound | 4.4 | 8.1 | 5.4 |

The above numbers are percentages of solids. The total solids in corpus callosum are 32, and in cortex 18 per cent. W. D. H.

Chemical Researches on the Thyroid and Parathyroids. JEAN CHENU and ALBERT MOREL (*Compt. rend.*, 1904, 138, 1004—1007).—The parathyroids in the dog contain only about a quarter the amount of iodine found in the thyroid. The rôle of the two organs is different, that of the thyroid being mainly exercised by the iodothyryn it produces. W. D. H.

Nucleo-proteid from the Pancreas. PHOEBUS A. LEVENE and LYMAN B. STOOKEY (*Zeit. physiol. Chem.*, 1904, 41, 404—406. Compare Abstr., 1903, ii, 438; Bang, Abstr., 1901, i, 299; Jones and Whipple, *ibid.*, 1902, i, 731).—A mixture of thymin and uracil has been isolated from the pancreatic nucleo-proteid, and it is thus probable that the proteid is a derivative of a complex nucleic acid, and not merely of guanylic acid, since this does not yield pyrimidine bases on hydrolysis. J. J. S.

Extensibility of Muscle. MOTONOSUKE GOTO (*Zeit. Biol.*, 1904, 46, 38—60).—The form of the extensibility curve of frog's muscles, especially after work, is independent of its excitability. The mechanical properties of muscle are influenced by substances which do not penetrate into the fibres. Extensibility depends on the muscular protoplasm, and also on the external structures (sarcolemma, perimysium). Internal friction and extensibility are two properties of muscle which alter independently of each other. Internal friction is influenced not only by the behaviour of the protoplasm, but also by the condition of the surface. It is necessary to distinguish between internal friction of the muscle-lymph, friction of connective tissue structures on one another, and friction between sarcolemma and protoplasm.

W. D. H.

The Amount of Iodine in Animal Cells. J. JUSTUS (*Chem. Centr.*, 1904, i, 1281; from *Virchow's Archiv*, 176, 1—10. Compare *Abstr.*, 1903, ii, 311).—The following numbers give the amount of iodine in various animal tissues in hundredths of a milligram per 100 grams of tissue or organ: (1) from the calf: thyroid, 105·3; horny substance, 100; thymus, 46·8; skin with hair, 42·9; testis, 39·8; lymph glands, 33·3; liver, 22; mammary gland, 22; spleen, 15; lung, 15; kidney, 10; brain, 6·4; yellow marrow, 0. (2) From man: thyroid, 976; liver, 121; kidney, 105; stomach, 98·9; skin, 87·9; nails, 80; prostate, 68·9; suprarenal, 63·6; lymph glands, 60; spleen, 56; testis, 50; pancreas, 43·1; uterus, 41·3; lung, 32; tendon, 20; small intestine, 11·9; adipose tissue, traces.

The high amount in horny tissues is regarded as noteworthy.

W. D. H.

Alcohol in Animal Organs. GEORG LANDSBERG (*Zeit. physiol. Chem.*, 1904, 41, 505—523).—Small quantities of alcohol are obtainable from many organs and tissues which are freshly removed from animals. The proportion in which it occurs varies from 1 in 11,000 to 1 in 33,000 parts. The source of the alcohol is uncertain. Unless bacterial action occurs, it is not increased by digesting with sugar.

W. D. H.

Catalase in Different Animal Tissues. F. BATTELLI and Mdle. L. STERN (*Compt. rend.*, 1904, 138, 923—924).—The power of tissues to decompose hydrogen peroxide is attributed by Loew to an enzyme catalase. This reaction may be studied quantitatively by estimation of the amount of oxygen liberated. In the present research, numbers are given for the liver, kidney, heart, muscles, &c., of a frog and guinea-pig; the latter animal gives the higher figures throughout. The liver contains by far the most catalase, and the brain the least; the amount of oxygen disengaged in the first five minutes by the liver was 295 (frog), 305 (guinea-pig); by the brain, 1·2 and 1·6 c.c. in the two animals respectively (0·1 gram of each organ was employed). Active metabolism does not necessarily imply much catalase; thus the figures given for the muscles are not much higher than those for the brain.

W. D. H.

Lævulose in Amniotic Fluid. AUGUST GÜRBER and D. GRÜNBAUM (*Chem. Centr.*, 1904, 1365; from *Münch. med. Woch.*, 51, No. 9).—The sugar in the amniotic fluid of the cow, goat, and pig is lævulose; it is especially abundant in the pig; in the allantoic fluid, it is also present, but here it is least abundant in the pig. In the human fluids, no sugar is present.
W. D. H.

The Membrane of Milk Globules. W. VÖLTZ (*Pflüger's Archiv*, 1904, 102, 373—414).—A review of previous work on the so-called haptogen membrane of milk globules, and a number of new experiments and analyses are given. The conclusion is drawn that such a membrane really exists, but its thickness and composition vary in different animals, and also in different stages of lactation in the same animal. They are regarded as very "labile." They consist of variable amounts of proteid, non-nitrogenous organic substances, and ash.
W. D. H.

Formation of Lactose in the Cow. CH. PORCHER (*Compt. rend.*, 1904, 138, 924—926. Compare this vol., ii, 424).—Further observations in reference to milk formation and glycosuria which confirm the hypothesis that lactose originates from the sugar brought to the mammary gland by the blood.
W. D. H.

Injection of Phloridzin in the Lactating Cow. CH. PORCHER (*Compt. rend.*, 1904, 138, 1457—1459).—The action of phloridzin on the mammary secretion is an indirect one; the smaller quantity of milk secreted contains a smaller total of lactose than before, although owing to concentration of the milk, its percentage is increased; this is a consequence of renal trouble that leads to diuresis and hypoglycæmia.
W. D. H.

Physiology of Glands. IV. LEON ASHER (*Zeit. Biol.*, 1904, 46, 61—76).—A critical discussion on researches on diuresis; it is largely polemical against O. Loewi and against the filtration theory.
W. D. H.

Indoxyl Pigments. LOUIS C. MAILLARD (*Zeit. physiol. Chem.*, 1904, 41, 437—454. Compare Abstr., 1902, i, 371; 1904, ii, 303).—Polemical. A reply to Ellinger and Bouma.
W. D. H.

Free Amino-acids in the Blood in Acute Atrophy of the Liver. CARL NEUBERG and P. F. RICHTER (*Chem. Centr.*, 1904, i, 1282—1283; from *Deutsch. med. Woch.*, 30, 499—501).—In a case of acute atrophy of the liver, 0.79 grams of tyrosine, 1.1 of leucine, and 0.24 of lysine were obtained from 345 c.c. of blood; this corresponds with 30 grams of free amino-acids in the whole blood. This was not due to proteolysis in the blood, for no proteolytic enzyme was discoverable there. It may be due to absorption from the intestine, or the breaking down of muscle proteid; another factor is lessened excretion, for the kidneys are comparatively inactive. The tyrosine separated spontaneously when the blood was kept.
W. D. H.

Albumosuria. GUSTAVE PATEIN and CH. MICHEL (*Compt. rend.*, 1904, 138, 1363—1365).—The Bence-Jones albumin, as it was formerly called, is regarded not as an albumose, but an albumin. W. D. H.

Autolysis of Animal Organs. ALBERT CHARRIN (*Compt. rend.*, 1904, 138, 1064—1067).—In various morbid conditions, the animal tissues lose much of their useful components, including enzymes, and waste materials are increased. W. D. H.

Pharmacological Action of Iodates, Bromates, Chlorates, other Oxidising Substances, and some Organic Drugs. ALBERT P. MATHEWS (*Amer. J. Physiol.*, 1904, 11, 236—249).—A discussion of the action of several compounds from the ionic point of view. W. D. H.

Intravenous Injection of Adrenaline (Epinephrine) and Peptone. WALTER W. HAMBURGER (*Amer. J. Physiol.*, 1904, 11, 282—302).—If the two substances are injected together, the rise of arterial pressure, due to adrenaline, occurs first, then the fall due to peptone. This takes place in whatever proportions the two are mixed. Peptone immediately following adrenaline does not affect the rise of pressure, but if the order is reversed, the fall due to peptone is checked, and a rise of pressure is seen.

The active "depressor" substance in pituitary extracts is soluble in alcohol, glycerol, and salt solutions, but not in ether. Repeated doses of the alcoholic extract produce always the same effect, but a second dose of the saline extract is ineffective unless a considerable interval elapses. The rise of pressure which follows the fall may be due to a "pressor" substance, or to the elimination of the "inhibitory" substance present in the saline extract. From experiments on the eye, the conclusion is drawn that adrenaline acts on muscular tissue and peptone on vaso-motor nerves. W. D. H.

Toxicity of Amylene Chlorohydrin (Stovaine). L. LAUNOY and F. BILLON (*Compt. rend.*, 1904, 138, 1360—1363).—This anæsthetic, in comparison with cocaine, is from a half to a third as toxic. It differs from cocaine by producing lowering of body temperature and vasodilatation at the point of injection. W. D. H.

Physiological Behaviour of some Camphor Derivatives. JULIUS W. BRÜHL [with RUDOLF KOBERT and RUDOLF GOTTLIEB] (*Ber.*, 1904, 37, 2178—2183).—Hydroxymethylenecamphor possesses weak bactericidal properties, but has none of the physiological action of camphor. Hydroxyethylidene- and hydroxypropylidene-camphors, on the other hand, exhibit the toxic properties of camphor.

α -Iodocamphor is feebly antiseptic, and irritates the mucous membrane. $\alpha\alpha$ -Di-iodocamphor is strongly irritant. C. H. D.

Properties of Solutions of Chloroform in Water, Saline, Serum, and Hæmoglobin. BENJAMIN MOORE and HERBERT E. ROAF (*Proc. Roy. Soc.*, 1904, 73, 382—412).—The action of the numerous substances used as anæsthetics probably depends on a general type of

interaction between it and the cell protoplasm. The present paper, however, relates to chloroform. Attention should not be restricted to the action of an anæsthetic on nervous structures; all cells (bacteria, amœbæ, ciliated cells, &c.) are equally affected. The action must therefore take place with some chemical constituent present in all varieties of protoplasm, and theories based on the high content of nerve cells in lecithin and fatty constituents may be disregarded. Proteid is the substance of all others universally present in all cells, and it is found that chloroform forms loose compounds with many proteids; if in excess, it will precipitate them. This explains the greater solubility of chloroform in the blood, or serum or hæmoglobin solutions, than in water or in saline solutions. Apparatus is described for determining such solubilities, and the results are given in tabular form. The loose compound of proteid-chloroform is compared to oxy-hæmoglobin. When anæsthesia occurs, the proteid-chloroform compound of the blood has parted with its chloroform to the cell-proteids. The compound there formed undergoes dissociation when the chloroform pressure is reduced on cessation of administering the anæsthetic, and anæsthesia thus ceases.

W. D. H.

Physiological Action of Radium Emanations. CHARLES BOUCHARD, PIERRE CURIE, and V. BALTHAZARD (*Compt. rend.*, 1904, 138, 1384—1387).—Mice and guinea-pigs confined in a vessel charged with radium emanations died in a few hours, respiration being earliest affected. Means were taken to remove the carbon dioxide formed, and to keep the oxygen supply constant. Death is not due to the ozone produced. *Rigor mortis* sets in early; there is congestion found in kidneys, liver, and brain, but especially in the lungs; the number of leucocytes is lessened. The tissues, especially of the body surface, are radioactive.

W. D. H.

Purification of Ricin and of Diphtheria-antitoxin. LUDWIG BRIEGER (*Chem. Centr.*, 1904, i, 1286; from *Festschr. zum 60 Geburtstag R. Kochs*, 1903, 364—381).—Two poisonous substances have been isolated from ricin by fractional precipitation with magnesium sulphate. The one which is precipitated contains albumin, whilst the other, which remains in solution, does not. Two samples of ricin were employed, of which one was Merck's and the other a preparation which had been obtained by extracting *Ricinus* seeds with potassium hydrogen carbonate and precipitating with ammonium sulphate. The latter had been kept 10 years, but had not lost any of its poisonous character. A dose of the precipitated substance of 0.1 mg. per kilogram of body-weight, when administered to rabbits, caused death in 24—48 hours, whilst a dose of the second substance of 1 mg. per kilogram of body-weight was fatal only after 4 days. Both substances cause agglutination of the red corpuscles of the blood; the insoluble substance resembles ricin in this respect, but the soluble substance is less effective. Attempts to purify ricin by means of papayotin and to cause the decomposition of the albuminous substance by bacteria both failed.

Experiments on the purification of diphtheria-antitoxin by Pröscher's method (German Patent 13757, June 21st, 1902) did not yield products free from albumin, the antitoxin being liable to putrefaction.
E. W. W.

Chemistry of Vegetable Physiology and Agriculture.

Action of Radium on Micro-organisms. ALAN B. GREEN (*Proc. Roy. Soc.*, 1904, 73, 375—381).—Numerous varieties of bacteria were exposed to the action of radium emanations; the extraneous micro-organisms in vaccine lymph were killed more rapidly than the specific vaccine virus. Non-spore-bearing bacteria exhibit least resistance. Increase of distance from the radium and interposition of screens of mica, glass, lead, and copper gauze weaken the action. After exposure at a distance of 1 mm. to the radium emanations for 24—120 hours, the micro-organisms show signs of radioactivity, and photographs are given which show their effect on a sensitised plate. This lasts for 3 months after exposure. The photographs appear to be caused by β -rays emitted by the organisms. W. D. H.

Reduction produced by Microbes. MARTINUS W. BEYERINCK (*Arch. Néerland.*, 1904, [ii], 9, 131—157).—The reduction of tellurates is best observed by employing the potassium salt. The group *Coli* and the vibrios are among the most active in this respect, whilst yeasts and mosses have no reducing action on tellurates. Various yeasts and *Oidium lactis* reduce molybdic acid.

Ferric organic salts are more suitable than ferrous salts for showing the production of sulphites and sulphides by aerobic microbes.

The production of hydrogen sulphide from sulphur, sulphites, and thiosulphates is readily effected by *Microspira desulfuricans* and *M. aestuarii*, as well as by many other microbes, both aerobic and anaërobic, especially by the group *Coli* and vibrios. An anaërobic bacterium (probably a *Thiobacillus*) was observed which produces hydrogen sulphide from sulphites and oxidises it to sulphur with slight aëration; it requires organic carbon.

Canal water contains two bacteria capable of reducing carbon dioxide. The one, *Thiobacillus thioparus*, obtains the necessary energy by the oxidation of hydrogen sulphide to sulphur; the other, *T. denitrificans*, by reducing nitrates to nitrogen. N. H. J. M.

Decomposition of Tellurium Salts by the Action of Micro-organisms. B. GOSIO (*Atti R. Accad. Lincei*, 1904, 13, i, 422—427).—Like arsenic compounds, those of tellurium are decomposed by moulds. Whilst, however, all arsenical compounds are attacked, but only by comparatively few species of hyphomycetes, of tellurium compounds, on the other hand, only certain undergo decomposition, but

this is carried out, with various degrees of readiness, by all the hyphomycetes examined. The action in the case of the tellurium compounds is much more rapid than with arsenic compounds, and, under favourable conditions, becomes apparent after two or three minutes.

A large number of bacteria were examined, and, in all but a few doubtful cases, decomposition of potassium tellurite took place.

From the author's experiments, it appears probable that the decomposition of tellurium compounds by micro-organisms is not brought about by means of products formed by the organisms, but is a direct consequence of the life or development of the moulds or bacteria.

T. H. P.

Production and Decomposition of Glycogen by Lower Vegetable Organisms. BERTHOLD HEINZE (*Centr. Bakt. Par.*, 1904, ii, 12, 43—78).—In addition to the known glycogen producing organisms, the author has found an alga, probably *Chlorella protothecoides*, and from dairy drainage a variety of *Prototheca* (probably Krüger's *Prototheca Beijerinckii*); also two soil organisms, provisionally termed Dematium-yeast and Dematium-mould. Provisional experiments with some leguminous bacteria (from *Vicia sativa*, *Vicia faba*, *Phaseolus vulgaris*, and *Pisum sativum*) indicated that considerable amounts of glycogen are formed in bacteroid-structures (compare Hiltner, *Arb. biol. Abt. K. Gesundheitamtes*, 3, 151—307).

As regards the production of glycogen by yeast in presence of suitable carbohydrates, pectin substances, and higher alcohols, it was found that conditions of temperature and aëration have a great influence, and that aspartic acid, ammonium carbonate, and lactic acid are favourable. The same conditions are also favourable to its production by the azotobacter-organisms.

N. H. J. M.

Histological and Chemical Changes in Flax Stems under the Influence of Microbes of Pectin- and Cellulose-fermentation. V. OMELIANSKI (*Centr. Bakt. Par.*, 1904, ii, 12, 33—43).—Flax stems subjected to the action of pectin-fermentation (flax rust) and cellulose-fermentation lost in weight 5.6 and 22.3 per cent. respectively. It was found that under the influence of pectin-fermentation all the pectin substances were destroyed, whilst the cellulose remained unchanged. In the case of cellulose-fermentation, most of the cellulose was destroyed, but not all, owing to the products having an injurious action on the fermentation process. The amount of xylan remained about the same in both cases.

N. H. J. M.

Ammonium Thiocyanate and Thiocarbamide as Sources of Nitrogen to Fungi and Micro-organisms. JOSEPH H. KASTLE and ELIAS ELVOVE (*Amer. Chem. J.*, 1904, 31, 550—557).—A nutritive solution containing ammonium thiocyanate as the nitrogenous food material is able to support the growth of *Penicillium glaucum*, whilst a similar solution in which the ammonium thiocyanate is replaced by thiocarbamide is unable to do so. It is found that the thiocarbamide is not poisonous to the fungus, but

that its nitrogen is not available for its growth. Potassium thiocyanate is also unable to supply the nitrogen required by the plant, and hence, in the case of ammonium thiocyanate, it is only the nitrogen of the ammonium radicle which is available for food.

Similar results were obtained with the various micro-organisms of putrid cheese and also with yeast. Thiocarbamide, although unable to furnish the nitrogen required for the growth and reproduction of the yeast, does not prevent alcoholic fermentation.

Ammonium thiocyanate slowly undergoes nitrification by the organisms of the soil, whilst thiocarbamide is either acted on extremely slowly or not at all. In this connection, it has been found that when thiocarbamide is treated with hydrogen peroxide, no nitrite is produced even in the presence of both calcium carbonate and manganous chloride, whilst ammonium thiocyanate yields an appreciable quantity of nitrite under these conditions.

E. G.

Leguminous Root-nodules. LORENZ HILTNER and RICHARD STÖRMER (*Bied. Centr.*, 1904, 33, 310—322; from *Arb. Biol. Abt. Land. u. Forstwirt.-K. Ges.-Amt.*, 1903, 3, 151 and 302).—In experiments in which the effect of inoculation with pure cultivations has been compared with soil, the results have shown that pure cultures are equal to, and generally better than, soil. Inoculation with soil is only suitable in the case of peat-land and with seeds which germinate rapidly. Seed inoculation may completely fail if the soil is at all dry, owing to the secretion of substances from the germinating seeds which check or destroy the infecting action of the bacteria. This is much more liable to occur with large seeds (lupins and peas, &c.) than with small seeds. The safest method is to let the seeds swell (not under water) before infecting. Even this method is, however, far from satisfactory. Better results were obtained, without previous swelling or germinating, by inoculating the seeds with bacteria in solutions of peptone or dextrose, or in milk. In this manner, the injurious effect of the substances secreted by the seeds is overcome.

N. H. J. M.

Influence of Metals on Fermenting Liquids. LEOPOLD NATHAN (*Centr. Bakt. Par.*, 1904, ii, 12, 93—94).—Apple must was less affected by metals than beer worts, although it dissolved more of the metal. German silver, copper, zinc, brass, bronze, and black iron were the most active in checking fermentation; then tin and lead. Polished iron, silver, nickel, gold, polished tin, and aluminium were indifferent or only slightly poisonous.

N. H. J. M.

Heat of Decomposition in Alcoholic Fermentation. MAX RUBNER (*Arch. Hygiene*, 1904, 49, 355—418. Compare *Abstr.*, 1901, ii, 304).—The heat of fermentation of sucrose was found to be 150·8 cal. (mean of six experiments with pure cultures). Pure maltose dissolved in beer worts and sown with 10 per cent. yeast gave 148·5 cal. as the heat of fermentation at 38°.

The results of eleven varying experiments with sucrose and maltose, with pure cultures and with growing yeast gave a mean of 149·5 cal.,

the extreme results being 2.47 above and -2.81 below the average. Differences in temperature (22—38°) had very little effect, but the amount of by-products may vary according to the rate of the fermentation.

The heat of inversion of sucrose was found to be 9.639 cal. per gram. or 3.293 Cal. per mol., which agrees with Stohman's calculation (+3.1 per mol.).

Leaving the inversion out of account, the results calculated for dextrose and for carbon dioxide (gas) are as follows: Dubrunfaut, 21.8; Brown, 21.4; Bouffard, 23.7; and Rubner, 25.6 Cal. The differences, although not inconsiderable, are less than those in results based on thermo-chemical measurements. N. H. J. M.

Velocity of Enzymatic Action. REGINALD O. HERZOG (*Zeit. physiol. Chem.*, 1904, 41, 416—424. Compare Abstr., 1904, ii, 164).—Further details concerning the mathematical relationships of enzymatic action and the influence on these of rapidity of diffusion are given. W. D. H.

Evolution of Free Nitrogen during Germination. NICOLA CASTORO (*Landw. Versuchs-Stat.*, 1904, 60, 41—62).—The results of experiments with *Phaseolus multiflorus*, *Pisum sativum*, *Lens esculenta*, *Zea Mais*, *Helianthus annuus*, *Tropaeolum majus* showed, in accordance with the earlier experiments of Lawes, Gilbert and Pugh, and Boussingault, that no appreciable evolution of free nitrogen took place during germination. Losses of nitrogen observed in isolated cases must be attributed to decomposition by bacteria. N. H. J. M.

Nitrogen Compounds in Non-germinated Seeds. ERNST SCHULZE and NICOLA CASTORO (*Zeit. physiol. Chem.*, 1904, 41, 455—473).—Small amounts of arginine have been extracted from the non-germinated seeds of *Lupinus luteus*, *Lupinus albus*, *Helianthus annuus*, *Triticum vulgare* (embryo), and *Arachis hypogaea* by Kossel and Kutscher's method. The conclusion is drawn that the arginine exists as such in the seeds and is not formed from more complex proteids during the extraction and subsequent treatment.

Tyrosine and asparagine could not be detected in the seeds of *Lupinus luteus*, but vernin (Abstr., 1886, 157) was isolated. This appears to be a glucoside, since, when hydrolysed with dilute sulphuric acid, it yields guanine and a sugar which reduces Fehling's solution, probably a pentose. When vernin is dissolved in sulphuric acid and mixed with α -naphthol, a red colour changing to violet is developed. Red colorations are also produced with phloroglucinol or resorcinol and hydrochloric acid.

Choline and betaine have also been isolated from seeds of *Helianthus annuus*, and choline, vernin, and tyrosine from *Arachis hypogaea*. J. J. S.

Inorganic Phosphates in Plant Seeds and in Seedlings. ERNST SCHULZE and NICOLA CASTORO (*Zeit. physiol. Chem.*, 1904, 41, 477—484).—The seeds of the following plants have been tested for

inorganic phosphates: *Lupinus angustifolius*, *Lens esculenta*, *Vicia Faba*, *Zea Mais*, *Picea excelsa*, *Pinus Laricio*, *P. Strobus*, *P. Cembra*. The method employed was as follows: the dried and finely divided seed was left for 2 hours in contact with 10 times its weight of 1 per cent. hydrochloric acid, the phosphates in the clear solution were precipitated by the addition of calcium chloride and ammonia solutions. The precipitate was extracted with ammonium citrate and the solution treated with magnesia mixture. In the case of *Pinus Strobus* only was a precipitate obtained and even here the amount was almost negligible. These results confirm those of Hart and Andrews (this vol., ii, 201).

Etiolated seedlings of *Lens esculenta*, *Vicia Faba*, and *Zea Mais*, when examined by the same method, were found to contain appreciable amounts of inorganic phosphates. J. J. S.

Intramolecular Respiration of Plants. EMIL GODLEWSKI (*Bul. Acad. Sci. Cracow*, 1904, 116—158).—Lupin seeds in pure water develop only a very slight intramolecular respiration when oxygen is excluded, but respiration acquires some vigour when some sugar fermentable by lupin seeds is added. The intramolecular respiration induced in this manner facilitates the hydrolisation of the reserve carbohydrates.

It is possible for lupin seeds to germinate in absence of oxygen when fructose is present, and less readily in presence of sucrose. The roots die after attaining a length of 3—6 mm.

During the intramolecular respiration of lupin seeds in sugar solutions, about 30 per cent. of the proteids are decomposed, the chief product being amino-acids. Asparagine is formed only in small quantities. This result accords with Palladin's observations with young wheat plants, and indicates, in connection with Schulze's theory, that, in absence of oxygen, a synthetical production of asparagine as commencement of proteid regeneration is impossible in the case of higher plants.

The decomposition of proteids in absence of oxygen is of interest as it seems to exhibit dissimilation apart from synthetical processes.

N. H. J. M.

Ready-formed Sugars of Malt. ARTHUR R. LING and THEODORE RENDLE (*J. Inst. Brewing*, 1904, 10, 238—261).—The soluble carbohydrates of malt include sucrose, invert sugar, maltose (?), pentoses, and gummy substances. They are formed chiefly during flooring, but a considerable amount of metabolism goes on during withering and the earlier stages of kilning.

The determination of the soluble carbohydrates of malt, based on digesting the ground malt with water at the ordinary temperature, gives high results, on account of the production of maltose by the action of the diastase on the starch granules during the extraction. This diastatic action may be avoided by extracting the malt with a solution containing 0.02 per cent. of potassium hydroxide or an equivalent amount of sodium hydroxide or ammonia. In this alkaline solution, the total soluble organic matter may be determined directly, whilst

the reducing sugars may be determined directly, and the sucrose indirectly, by the cupric reduction method. In the absence of precise knowledge concerning the nature of the reducing sugars, their amount may be expressed as invert sugar. Other circumstances being the same, the percentage of soluble carbohydrates is higher in a forced malt than in one not forced, but even when the amount of these carbohydrates is calculated on the dry malt, it is as yet impossible to fix a definite limiting value for non-forced malts. In pronounced cases of forcing, the sucrose and apparent invert sugar may constitute over 12 per cent. of a malt. The amount of soluble carbohydrates in a malt is reduced by respiration, both aerobic and anaerobic. Pneumatic malt appears to contain less soluble carbohydrates, other than sucrose and invert sugar, than floor malts. The amount of soluble carbohydrates probably varies with the kind and condition of the barley.

T. H. P.

Formation of Oxalic Acid in Green Plants. WILHELM BENECKE (*Bied. Centr.*, 1904, 33, 387—389; from *Bot. Zeit.*, 1903, 79, and *Naturw. Rundschau*, 1903, 18, 540).—Oxalate is produced in maize plants grown with nitrate, but not when an ammonium salt is employed as the source of nitrogen. In the case of other plants (*Oplismenus*, *Fagopyrum*, and *Tradescantia*), complete freedom from calcium oxalate could not be attained, but the amount stored up in the plants depended largely on the character of the nutritive solution, being increased by nitrates and diminished by ammonium salts. This is due to the nitrate leaving a basic, and the ammonium salt an acid, residue, and by addition of magnesium carbonate, for example, to the solution containing an ammonium salt, the amount of oxalate in the plants is made to approach nearly, or quite, that accumulated under the influence of a nitrate. Algæ are not similarly influenced.

N. H. J. M.

The Saponifying Power of the Castor Oil Bean. MAURICE NICLOUX (*Compt. rend.*, 1904, 1175—1177).—It is well known that the bean of the castor oil plant is capable of saponifying fats and oils in the presence of free acid. Hitherto this action has been ascribed to the presence of a ferment; it is now shown, however, to be due to the cytoplasm of the bean.

S. S.

Occurrence of Aliphatic Alicyclic Compounds in Plants. HERMANN KUNZ KRAUSE (*J. pr. Chem.*, 1904, [ii], 69, 385—386).—See this vol., i, 587.

Composition of some Papilionaceæ at Different Stages of Growth. W. G. SÖDERBAUM (*Bied. Centr.*, 1904, 33, 322—326; from *Meddel. kong. landtbr. akad. exper.*, No. 70, 1—20, *Stockholm*, 1903).—Analyses of *Astragalus glycyphyllus*, *Lathyrus pratensis*, *Medicago sativa*, *Melilotus alba*, *Orobis niger*, *Trifolium pannonicum*, and *Vicia dumetorum* were made at four dates, June 7 and 21, July 5, and August 15. The total nitrogen diminished, but with decreasing rapidity, during the two months. The amide-nitrogen, as percentage of

total nitrogen, diminished throughout the whole period in two cases (*Medicago* and *Vicia*), whilst in three cases there was a rise from the second to third period. The digestible proteids in the dry matter showed in some cases an uninterrupted fall, and in others a rise from the third to the fourth period.

The whole series of results shows that the amounts of the different constituents undergo very rapid changes, influencing the nutritive value of the various plants, and that the different plants of the same family vary considerably in this respect.

N. H. J. M.

Nature of the Principal Phosphorus Compound in Wheat Bran. A. J. PATTEN and EDWIN B. HART (*Amer. Chem. J.*, 1904, 31, 564—572).—When wheat bran is extracted with 0.2 per cent. hydrochloric acid and the filtered solution is treated with 95 per cent. alcohol, a voluminous, flocculent precipitate is obtained which, when dried at 110°, forms a white, amorphous powder, readily soluble in water. The aqueous solution of this substance is acid to litmus, and on addition of solutions of metallic salts, the compound is reprecipitated. This compound is the magnesium calcium potassium salt of an acid, $C_2H_8P_2O_6$, which is probably identical with the anhydro-oxy-methylenediphosphoric acid described by Posternak (*Abstr.*, 1903, ii, 680). Its alkali salts are freely soluble in water, the calcium and copper salts are slightly so, whilst the barium and strontium salts are but sparingly soluble. The acid and its salts appear to be widely distributed in the vegetable kingdom.

E. G.

Influence of Lime and Marl on the Yield of Vetches. RICHARD ULBRICHT (*Landw. Versuchs-Stat.*, 1904, 60, 135—146).—Notwithstanding the small amounts of calcium and magnesium in the soil, the application of phosphoric acid, potassium, and very little nitrogen resulted in the highest yield. Burnt marble (= 500 kilos. CaO per morgen) somewhat increased the yield, whilst twice that amount caused a considerable reduction in the yield. Magnesite, in conjunction with lime (= 250 kilos. CaO), did not reduce the yield as compared with the same amount of lime alone, but when applied in conjunction with a larger quantity of lime (= 500 kilos. CaO) it had a distinctly injurious effect, the injury increasing with the amount of magnesite.

Heavy applications of burnt dolomite were found to be injurious, but had less effect than the corresponding amounts of lime and magnesia in a mixture of burnt marble and magnesite.

N. H. J. M.

Icelandic Fodder Plants. ST. STEFANSEN and W. G. SÖDERBAUM (*Bied. Centr.*, 1904, 33, 394—397; from *Meddel. kongl. landtbruks. akad. exper.*, No. 77, *Stockholm*, 1903. Compare *Abstr.*, 1893, ii, 592, and 1892, ii, 187).—Of the 360 flowering plants known in Iceland, 25 per cent. are grasses or sedges. Analyses are given of twenty-five of the most important plants, collected in July or early in August. As regards the gramineous herbage, the results show higher percentages of ash and nitrogenous matter and lower percentages of

cellulose than the corresponding Swedish varieties, and the digestibility of the nitrogenous matter is also relatively higher. The composition of the sedges did not differ essentially from those analysed in Sweden, except that the digestibility of the nitrogenous matter is greater in the Icelandic specimens.

N. H. J. M.

Composition of Potatoes. EINAR FORFANG (*Bied. Centr.*, 1904, 33, 392—393; from *Tidsskr. Norsk. Landbr.*, 1903, 10, 151—162).—The average composition of ten varieties of potatoes grown in West Norway was as follows: dry matter, 24.42; starch, 15.15; sugar, 2.16; crude fibre, 0.66; furfuroids, 0.667; total N, 0.399; fat, 0.04; and ash, 0.98 per cent.

N. H. J. M.

Poultry Feeding. FRITZ LEHMANN (*Bied. Centr.*, 1904, 33, 417—419; from *Landw. Jahrb.*, 1903, *Erg.-bd.*, iv, 137).—It was found, in accordance with earlier results, that crude fibre is not digested by birds. In absence of sufficient data derived from experiments with poultry, digestibility-coefficients obtained in pig-feeding experiments should be employed, although it is possible that the digestive power of poultry is somewhat less than that of pigs.

N. H. J. M.

Presence of Nitrates in Wines. W. SEIFERT and HERMANN KASERER (*Bied. Centr.*, 1904, 33, 345—347; from *Zeit. Landw. Versuchswes. Oesterr.*, 1903, 6, 555).—A number of samples of must, fermented with pure yeast, were found to contain nitrates. The absence of nitrates in some wines may be partly due to greater ripeness of the grapes, or to conditions of soil, manuring, and climate. It is, however, shown that wines which contain nitrates may fail to give a reaction with diphenylamine unless heated for some minutes with blood-charcoal.

N. H. J. M.

Experiments with Molasses Manure. HENRIK G. SÖDERBAUM (*Bied. Centr.*, 1904, 33, 307—310; from *Meddel. kongl. landtbruks. akad. exper.*, No. 77, *Stockholm*, 1903).—The preparation employed was a dark brown powder having a distinct odour of beet molasses. It contained CaO, 10.35; K₂O (soluble in water), 10.07; SO₃, 16.65; organic nitrogen, 2.81; and 49.35 per cent. of non-nitrogenous organic matter.

The results of manurial experiments showed that for barley it was somewhat more effectual than potassium sulphate; for oats, equal to sodium nitrate containing the same amount of nitrogen, and for potatoes equal as regards yield to kainite, without causing a depression in the amount of starch.

N. H. J. M.

Activity of the Phosphoric Acid in Various Phosphates. OSKAR BÖTTCHER (*Bied. Centr.*, 1904, 33, 379—382; from *Illust. landw. Zeit.*, 1903, 23, 1063. Compare *Abstr.*, 1903, ii, 750).—The various phosphates had very little after-effect and must be classed with the sparingly soluble phosphates which are not suitable substitutes for basic slag on ordinary (non-acid) soils. As regards basic slag, the

after-effect of the two samples employed showed, as the first crop did, that the solubility in citric acid is the most important characteristic.

N. H. J. M.

Decomposition of Crude Phosphates for Manurial Purposes.

A. YSTGAARD (*Bied. Centr.*, 1904, 33, 419—422; from *Tekn. Ugebl.*, 50, 329—332; and *Tidsskr. norsk. Landbr.*, 1903, 10).—When a mixture of apatite and carnallite acid finely powdered) is heated for 10—15 minutes at 700—800°, a product is obtained in which 80 per cent. of the total phosphoric acid is soluble in 2 per cent. citric acid. More prolonged heating is to be avoided, as the magnesium phosphate first found is transformed into less soluble phosphates. The highest amount of soluble phosphate is obtained when a considerable excess of carnallite is employed. This, of course, lowers the percentage of total phosphoric acid and is objectionable in other respects. The most suitable mixture was found to be apatite, 100; carnallite, 200; and kieserite, 100 parts. The product then contains P_2O_5 , total 20.71; soluble in 2 per cent. citric acid, 15.23; Cl, 16.47; SO_3 , 19.76; CaO, 9.22; MgO, 10.20; K_2O , 6.85; and Na_2O , 1.45 per cent. Other crude phosphates may be similarly treated.

Pot experiments with oats and peas showed that the new phosphates gave better results than basic slag, being particularly favourable to seed production. This is attributed to the phosphoric acid being present as magnesium salt, and to the favourable relation, in the manure, between calcium and magnesium.

N. H. J. M.

Analytical Chemistry.

A Simple Extractor. A. COPPALLE (*Ann. Chim. anal.*, 1904, 9, 161—162).—The apparatus, which is readily put together and acts like a Soxhlet apparatus, consists of a round-bottomed flask attached to a pear-shaped vessel which, in turn, is connected vertically with a condenser.

Inside the pear-shaped vessel is placed a small glass or porcelain disc, 4 or 5 millimetres thick, and furnished with two holes. This plate serves as support for a rather narrow glass funnel containing a small filter, or for a filtering tube containing asbestos or cotton-wool; the other opening admits the vapours. The substance is placed in the tared funnel or filtering tube and may be reweighed after the extraction is finished.

If the distillation is well regulated, the substance to be extracted is always covered with the solvent, and the extraction is accelerated by the constant falling of drops from the condenser. To insure the complete immersion in the solvent of the sample in all cases, the funnel may be provided with a tube bent into a S-shape which acts as a siphon as soon as the solvent has quite covered the filter and its contents.

L. DE K.

Filtration and Ignition of Gelatinous Precipitates. MAX DITTRICH (*Ber.*, 1904, 37, 1840—1842).—For the filtration of gelatinous precipitates, such as aluminium or iron hydroxides, the following method is recommended. Before the filtration of the precipitate, filter paper, which has been disintegrated by vigorous shaking with water in a test-tube, is added. The filtration and washing of the precipitate can then be carried out much more quickly than by the usual method, since the precipitate no longer forms a gelatinous mass adhering to the sides of the filter and closing its pores. In burning precipitates treated in this manner, special care must, however, be taken that the combustion of the filter paper is complete. After ignition, the residue does not consist of hard lumps, but is a finely-divided powder. In estimating iron as oxide by this method, there is no danger of any reduction taking place during the ignition.

The advantage of the method is pointed out in several examples, as when aluminium hydroxide has to be redissolved to free it from alkali, or during the separation of iron and alumina. A. MCK.

***p*-Nitrophenol as Indicator.** LEOPOLD SPIEGEL (*Zeit. angew. Chem.*, 1904, 17, 715—716).—A reply to Lunge on the use of *p*-nitrophenol instead of methyl-orange as indicator. Lunge used a 0.2 per cent. solution of this indicator, whereas a 2.5 per cent. solution should have been employed.

The author withdraws a former statement that fused borax should behave differently to the crystallised salt with either *p*-nitrophenol or methyl-orange. L. DE K.

Ionisation Constants of Phenolphthalein and the Use of this Substance as an Indicator. HERBERT N. MCCOY (*Amer. Chem. J.*, 1904, 31, 503—521).—When phenolphthalein is used in the titration of sodium carbonate solution, it is found that the quantity of acid required to discharge the colour is dependent on the amount of the indicator present. On account of this fact, it occurred to the author that by determining the ionisation constant of phenolphthalein a method might be obtained for estimating the alkalinity of solutions of sodium hydrogen carbonate. Experiments have been made in which measured quantities of ammonia, phenolphthalein, and ammonium chloride, each in *N*/10 solution, were added successively to 80 c.c. of pure water, the mixture being afterwards diluted to a total volume of 100 c.c.; the concentration of the salt formed was determined by comparing the colour of the solution with that of a solution containing 1 c.c. of *N* sodium hydroxide diluted to 100 c.c. with *N*/12,000 phenolphthalein. From the results of these experiments, the average value of *K* was found to be 1.6×10^{-4} .

It is pointed out that, the value of this ionisation constant being known, the degree of accuracy with which it is possible to titrate any acid or base of known ionisation constant can be easily calculated from a consideration of the end of the reaction from the standpoint of chemical equilibrium. It is found that phenolphthalein is an excellent

indicator for almost all acids, including the so-called weak acids, but is not applicable to the weakest bases, although it can be used with many of the amines and other moderately weak bases.

It is well known that the addition of a large excess of alkali to a slightly alkaline solution of phenolphthalein causes a great diminution in colour. To explain this, it is suggested that the red salt is also an extremely weak acid which is converted into the corresponding colourless salt only by the addition of a large excess of the base. In conclusion, the question is discussed from the point of view of the constitution of phenolphthalein and its salts.

E. G.

Hydrochloric Acid as a Standard Titration Liquid. W. A. ROTH (*Zeit. angew. Chem.*, 1904, 17, 716—717).—Raschig (this vol., ii, 441) has proposed to prepare a hydrochloric acid of exactly known composition by passing dry hydrogen chloride into a known weight of water and reweighing. The author has also used hydrochloric acid in volumetric analysis, but prefers to ascertain the exact strength of the acid by means of a gravimetric estimation as silver chloride. It should be remembered that silver chloride should be washed with iced water as it is not altogether insoluble at a somewhat higher temperature.

L. DE K.

Estimation of Chlorides in Urine. JULES VILLE and EUGÈNE DERRIEN (*Bull. Soc. chim.*, 1904, [iii], 31, 581—585).—The authors have made a comparative study of the various methods of estimating chlorides in urine. The processes examined were Mohr's direct method, in which the urine diluted with ten times its weight of water is titrated with a standard solution of silver nitrate, using potassium chromate as an indicator, and various modifications of this in which the organic matter is first destroyed by ignition of the solid residue with sodium carbonate and potassium nitrate (Mohr) or by treatment with potassium permanganate (Denigès) or lead dioxide (Loubiou, *Abstr.*, 1899, ii, 72), or in which its action on the silver nitrate is prevented by the addition of sodium acetate and acetic acid (Freund and Toepfer, *Abstr.*, 1894, ii, 260), and Charpentier's process in which the titration is made in presence of nitric acid, ammonium thiocyanate and a ferric salt being used as indicators. They find that Mohr's direct process and the Freund-Toepfer modification give almost identical results, which, with urines of sp. gr. greater than 1.010, are higher than the results obtained with the other processes examined. This difference is due to the influence of the organic matter, and its magnitude is proportional in normal and albuminous urines to the density, increasing by 0.07 for every increment of 0.001 in the sp. gr. of the urine. In urines containing dextrose, this relation also holds provided that the sp. gr. of the dextrose-free liquid is taken for comparison. These results show that Mohr's direct process may be employed in estimating chlorides in urines of sp. gr. less than 1.010 and in others also provided these are suitably diluted and, where necessary, a correction for the influence of dextrose on the density is made.

T. A. H.

Forms in which Sulphur occurs in Coal; their Calorific Values and their Effects on the Accuracy of the Heating Powers, calculated by Dulong's Formula. E. E. SOMERMEIER (*J. Amer. Chem. Soc.*, 1904, 26, 555—568).—The estimation of the calorific value of coal from the ultimate analysis involves the calorific value of the sulphur present. When the amount of sulphur is large, the question is important, especially as to how the heating value is affected by the different forms in which sulphur may occur. The author has studied the question experimentally.

Since pyrites does not burn completely in a calorimeter, the samples used were burned with coal. As an average of three determinations with one sample and four with another, the value 2637 cal. for 1 gram of pyrites was obtained. With 53.2 per cent. of sulphur in the pyrites, the calorific value per gram of sulphur as pyrites is 4957 cal.; 2915 cal. is the heat of combustion of 1 gram of sulphur as pyrites under ordinary conditions of combustion.

A. McK.

Estimation of Sulphur in Oils, Bitumens, and Coals. EDMUND GRAEFE (*Zeit. angew. Chem.*, 1904, 17, 616—619).—The substance, if liquid, is poured on to a little cotton-wool contained in a perforated conical platinum vessel, and the increase in weight is recorded. Coals and bitumens are either taken in lump or in a compressed state. The whole is suspended in a bottle previously filled with pure oxygen and also containing a solution of sodium peroxide. The charge is fired by electricity, the conducting wires being made of copper. The sulphuric acid formed in the combustion is then estimated as usual in the alkaline solution.

L. DE K.

Action of Sodium Nitroprusside on Alkalis, Carbonates, Hydrogen Carbonates, and Ammonia. C. REICHARD (*Zeit. anal. Chem.*, 1904, 43, 275—279).—A very dilute solution of sodium or potassium hydroxide, mixed with sodium nitroprusside, develops a yellow coloration. No such effect is produced by sodium or potassium carbonate; on the contrary, the addition of a normal or acid alkali carbonate to the yellow mixture reduces the depth of the colour, or in large excess destroys it altogether. The action of ammonia is somewhat similar to that of the alkali hydroxides, but a very much stronger solution is required to produce the yellow colour.

M. J. S.

Estimation of Nitrogen in Foods and Physiological Products. HENRY C. SHERMAN, C. B. McLAUGHLIN, and EMIL OSTERBERG (*J. Amer. Chem. Soc.*, 1904, 26, 367—371).—A series of experiments showing that the Kjeldahl process in its various modifications is not always completed when the acid mixture has been boiled until colourless. The following modification gives satisfactory results with proteid and related compounds. The sample is heated with 20 c.c. of sulphuric acid and 0.7—1 gram of mercury until frothing ceases; 10—15 grams of potassium sulphate are added, and the whole is then boiled as usual. After some 30 minutes, the mixture is generally colourless, but the boiling should then be continued for at least another half hour.

L. DE K.

Sprengel's Method for the Colorimetric Estimation of Nitrates. LAUNCELOT W. ANDREWS (*J. Amer. Chem. Soc.*, 1904, 26, 388—390).—The product formed in the action of Sprengel's reagent (phenol-*p*-sulphonic acid with excess of sulphuric acid) on small quantities of nitrates appears to be *o*-nitrophenol-*p*-sulphonic acid. As in alkaline solution this compound shows the same depth of colour as *p*-nitrophenol, a standard comparison liquid for Sprengel's process may be conveniently made by dissolving 0.993 gram of *p*-nitrophenol in a litre of water; 1 c.c. of this represents 0.1 mg. of nitrogen. For use, a definite amount is taken and rendered alkaline with potassium hydroxide. L. DE K.

Analysis of Sodium Nitrite. GEORG LUNGE (*Chem. Zeit.*, 1904, 28, 501—502).—Schultz has modified his process for the titration of sodium nitrite by means of sodium sulphanilate, the end reaction being now ascertained by an immediate reaction on potassium iodide-starch paper, which should persist for a few minutes. Although the author agrees that, with care, good results may be obtained, he still prefers for commercial disputes his permanganate process. In this process, the solution of the nitrite (23 grams per litre) is added from a burette to 45 c.c. of *N*/2 permanganate diluted with 400 c.c. of water at 40° and acidified with sulphuric acid. The permanganate must be standardised with technically pure sodium nitrite. The end reaction is shown by the complete decolorisation of the liquid. L. DE K.

Estimation of Phosphoric Acid as Magnesium Pyrophosphate. K. K. JÄRVINEN (*Zeit. anal. Chem.*, 1904, 43, 279—282).—If phosphoric acid is precipitated with magnesia mixture under unsuitable conditions, an error either of excess or deficiency, which may reach 3 per cent., may be incurred. The following procedure will insure an exact result—The phosphate solution is mixed with ammonia until the odour can just be detected. The solution is then poured slowly, and with stirring, into a neutral mixture of magnesium chloride and ammonium chloride (10 c.c. for 0.1 gram of phosphoric oxide of a solution containing 102 grams of magnesium chloride and 53 grams of ammonium chloride per litre). The free ammonia in the phosphate solution should be completely absorbed by the formation of the precipitate; should the mixture thereafter smell of ammonia, some trimagnesium phosphate will be formed. A 0.5 per cent. solution of ammonia is now to be added very slowly until the mixture has a strong ammoniacal odour, and finally 1/3 the volume of 10 per cent. ammonia. Filtration may take place after 2 hours, and if the filter is burnt apart from the precipitate the latter will be obtained perfectly white and of constant weight after a single ignition. M. J. S.

Estimation of Minute Quantities of Arsenic in Copper Ores and Metallurgical Products. THOMAS C. CLOUD (*J. Soc. Chem. Ind.*, 1904, 23, 524—526).—The ore is digested with sulphuric and nitric acids on a water-bath until decomposed. The solution is then evaporated and heated on a sand-bath until nearly all excess of sulphuric acid has been removed. When cool, the residue is dissolved

in water, filtered, and the copper in the filtrate deposited electrolytically. The electrolysis is stopped whilst the solution still contains from 0.05 to 0.08 gram of copper, a previous estimation of the copper in another portion of the ore having been made. The solution, together with all the deposit on the anode, is evaporated to a small volume and gradually introduced into a Marsh apparatus. The tube containing the mirror of arsenic is cut off at the end of the operation and weighed. After dissolving the mirror in nitric acid, the tube is washed, dried, and reweighed, the difference between the two weighings giving the amount of arsenic.

W. P. S.

Determination of the Calorific Power of Blast-furnace Gases by means of the Calorimetric Bomb. GEORGES AETH (*Bull. Soc. chim.*, 1904, [iii], 31, 576—578).—The author points out that Mahler's calorimetric bomb (*Abstr.*, 1892, 260) is unsuited to the determination of the calorific value of mixtures of combustible gases owing to practical difficulties of manipulation and to the smallness of the rise in temperature which could be obtained even under the best conditions. He suggests instead that the maximum calorific value should be calculated after the composition of the mixture has been ascertained by analysis.

T. A. H.

Use of Sodium Peroxide in the Qualitative Analysis of Organic Substances. HANS H. PRINGSHEIM (*Ber.*, 1904, 37, 2155—2156. Compare this vol., ii, 146).—The ignition of organic substances with sodium peroxide may be employed for the rapid and simultaneous qualitative detection of the halogens, phosphorus, arsenic, and sulphur. A mixture of sodium peroxide with 1/25th part of an organic, non-hygroscopic substance, such as naphthalene or cinnamic acid, is prepared and stored. The substance to be tested is added to a small quantity of this mixture in an iron vessel, and heated until the reaction occurs. The mass is then dissolved in water, and the elements named are tested for in the usual manner.

C. H. D.

Volumetric Method for the Estimation of Carbon Dioxide. THOMAS MACARA (*Analyst*, 1904, 29, 152—153).—The process is based on the fact that barium carbonate behaves like an alkali towards methyl-orange. A known quantity of the sample is placed in a flask provided with a tapped funnel and a delivery tube. The latter passes into a second flask containing saturated barium hydroxide solution. By the addition of hydrochloric acid to the evolution flask and subsequently boiling the contents, all the carbon dioxide is driven off, and absorbed in the second flask. The excess of free barium hydroxide in the latter is then neutralised with $N/2$ hydrochloric acid, using phenolphthalein as indicator. Methyl-orange is added and the barium carbonate titrated with $N/10$ hydrochloric acid. The usual precautions are necessary when hydrogen sulphide, sulphur dioxide, chlorine, bromine, or oxides of nitrogen are present in the sample.

W. P. S.

Portable Outfit for the Estimation of Carbon Dioxide, Dissolved Oxygen, and Alkalinity in Drinking Water. FRED B. FORBES (*J. Amer. Chem. Soc.*, 1904, 26, 382—388).—A fully illustrated arrangement for testing waters, suitable for field work. The estimations are made by the usual processes. L. DE K.

Action of Sodium Picrate on Sodium Carbonate Solutions. C. REICHARD (*Zeit. anal. Chem.*, 1904, 43, 269—275).—Sodium carbonate seems to possess a specific property of precipitating sodium picrate from solution. A single drop of a cold saturated solution of the picrate added to 10 c.c. of a 1 per cent. solution of the carbonate produces a slight turbidity, and with increasing concentration of the carbonate solution, or larger quantities of the picrate, the phenomenon becomes still more conspicuous. Sodium hydrogen carbonate, sodium phosphate, and sodium sulphate exhibit no such effect, but their presence even in relatively large quantities does not inhibit the action of the normal carbonate. M. J. S.

Volhard's Silver Estimation. COPIUS HOITSEMA (*Zeit. angew. Chem.*, 1904, 17, 647—650).—An adverse criticism on Rose's improved Volhard's process (*Trans.*, 1900, 77, 232). Although this modification has rendered the reaction more sensitive, it has not improved the accuracy of the process, as the precipitated silver thiocyanate retains free silver nitrate or potassium thiocyanate. L. DE K.

Estimation of Calcium. ENGELBERT KETTLER (*Zeit. angew. Chem.*, 1904, 17, 685—686).—A process devised for operators who have only spirit lamps at their disposal. The calcium oxalate, obtained in the usual manner, is ignited to carbonate, which is then dissolved in a sufficiency of dilute hydrochloric acid and precipitated by adding dilute sulphuric acid and four times the bulk of absolute alcohol. The calcium sulphate is then collected, washed with alcohol, dried, and ignited, the filter being burnt separately. L. DE K.

Estimation of Molybdenum and Tungsten and their Separation from Mercury by the Aid of Hydrazine. PAUL JANNASCH and W. BETTGES (*Ber.*, 1904, 37, 2219—2228).—Mercury may be readily separated from molybdenum (in the form of a molybdate) by reduction with hydrazine sulphate in the presence of tartaric or citric acid (2—3 grams) at 80°. The precipitated mercury is then dissolved and estimated as sulphide. Mercury may also be separated from tungsten (as tungstate) by precipitation with an ammoniacal solution of hydrazine sulphate at 70—80°. The addition of citric or tartaric acid is not necessary.

Tungsten may readily be estimated in tungstates by precipitating as the trioxide with hydrazine chloride in the presence of free hydrochloric acid. J. J. S.

Separation of Manganese. OTTO FOERSTER (*Chem. Zeit.*, 1904, 28, 457—459).—When estimating manganese in the ashes of plants or in soils by means of the persulphate process, or by means of hydro-

gen peroxide, it is, according to the author, very essential to first remove any phosphoric acid; this may be done conveniently by either the tin, mercury, or molybdate method.

L. DE K.

Separation of Iron and Zirconium and other Metals by means of Nitroso- β -naphthol. GEORG VON KNORRE (*Zeit. angew. Chem.*, 1904, 17, 641—647, 676—678).—Iron may be quantitatively separated from zirconium by means of nitroso- β -naphthol. The precipitate, after being washed, is at once gradually ignited and so converted into oxide. In the presence of oxalic acid, the iron is not precipitated unless some hydrochloric acid is added to the hot solution. Tartaric acid, on the other hand, does not interfere with the precipitation.

The zirconium, also aluminium, chromium, &c., may then be estimated in the filtrate after destroying the organic matters by means of hydrochloric acid and potassium chlorate.

L. DE K.

Estimation of Minute Quantities of Bismuth in Copper and Copper Ores. THOMAS C. CLOUD (*J. Soc. Chem. Ind.*, 1904, 23, 523—524).—The colorimetric method proposed is based on the fact that lead iodide, when precipitated in the presence of bismuth, assumes a more or less red tint. The solutions employed consist of (a) bismuth nitrate, prepared by dissolving pure bismuth oxide in nitric acid and diluting so that 1 c.c. is equivalent to 0.0001 gram of bismuth; (b) lead nitrate, made by dissolving 6 grams of pure lead in nitric acid, evaporating, and diluting to 1000 c.c.; (c) 35 grams of potassium iodide in 4000 c.c. of water. A suitable quantity of the metallic copper under examination is dissolved in nitric acid and neutralised by the cautious addition of sodium carbonate, so that only a small precipitate is produced. After 3 hours, the solution is filtered, the precipitate is dissolved in dilute hydrochloric acid, and reprecipitated with hydrogen sulphide. The precipitate so obtained is dissolved in nitric acid and diluted to 250 c.c. One hundred and twenty-five c.c. are treated with 5 c.c. of the lead solution, the mixture is neutralised with ammonia and ammonium carbonate and finally ammonia are added in excess. After warming, the precipitate is collected on a filter, and washed with ammonium carbonate solution until free from copper. The precipitate is then dissolved in nitric acid, evaporated, taken up with water and nitric acid, and transferred to a graduated cylinder. The coloration produced on adding 25 c.c. of the potassium iodide solution is compared with that obtained with known quantities of the bismuth nitrate and lead nitrate solutions. The contents of the cylinders are well mixed, and the final comparison is made after the lapse of 20 minutes.

In the case of copper ores, the latter are dissolved in a mixture of nitric and sulphuric acids, evaporated, treated with water and a drop or two of hydrochloric acid, and filtered. The solution is now treated with hydrogen sulphide and the process completed as described for metallic copper.

It is stated that 0.00001 gram of bismuth can be estimated by this method.

W. P. S.

Estimation and Separation of Platinum from Potassium Sodium, Barium, Strontium, Calcium, Magnesium, Manganese, Tungsten, Cobalt, Nickel, Copper, Zinc, and Cadmium in Ammoniacal Solution by means of Hydrazine. PAUL JANNASCH and C. STEPHAN (*Ber.*, 1904, 37, 1980—1992. Compare Abstr., 1899, ii, 59).—On gradually adding ammonia to a boiling solution of potassium platinichloride containing hydrazine hydrochloride, the platinum is quantitatively precipitated in the metallic state; the potassium can be estimated in the filtrate. A similar separation can be effected in the case of a mixture of potassium platinichloride with a calcium, strontium, barium, or magnesium salt, but when a zinc or cadmium salt is used, part of the platinum remains in solution; in the case of zinc, 50—70 per cent., and in that of cadmium 40—60 per cent., of the platinum is precipitated. When a manganese salt is present, part of the manganese is precipitated as oxide, but by dissolving this away from the platinum by means of hot nitric acid containing hydrogen peroxide, correct values are obtained for the platinum. Platinum can be separated quantitatively from tungstic acid by means of hydrazine, but molybdic acid undergoes reduction to lower oxides in such a manner as to render the estimation of platinum impracticable. Nickel is partly, and cobalt nearly, completely reduced to the metallic state simultaneously with the platinum, whilst copper is quantitatively precipitated as metal; in all three cases, the co-precipitated metal can be dissolved away from the platinum by means of nitric acid, and the estimation of both metals made possible. In presence of a cyanide, the precipitation of platinum is always incomplete. W. A. D.

Estimation of Palladium and Separation from other Metals by means of Hydrazine. III. PAUL JANNASCH and W. BETTGES (*Ber.*, 1904, 37, 2210—2219. Compare Abstr., 1899, ii, 59, and preceding abstract).—The product obtained by the reduction of palladium salts with hydrazine sulphate and subsequent ignition, is a mixture of oxides which may be reduced to the metallic state by heating in a current of hydrogen. Palladium may be estimated by this process when the precipitation is carried out in a hot solution acidified with about 20 drops of dilute hydrochloric acid, the precipitate collected on a funnel-shaped asbestos filter tube, dried, and reduced.

No reduction occurs when the hydrazine is used at the ordinary temperature. Palladium may be separated from potassium, sodium, magnesium, zinc, and iron by similar methods, and these metals may then be estimated in the filtrates. In the case of magnesium and zinc, it is not necessary to destroy the excess of hydrazine sulphate used in the precipitation of the palladium. J. J. S.

Iodine Absorption as a Factor in the Examination of Otto of Roses. FREDERICK HUDSON-COX and WILLIAM H. SIMMONS (*Analyst*, 1904, 29, 175—178).—Twenty samples of otto of roses, which had previously been examined by the ordinary methods and found to be of good quality, gave iodine values (Hübl) varying from 187 to 194. Several samples of artificial otto and of oils used as adulterants gave iodine values of well over 200, geranium oil being the lowest with a

value of 213. Citral and citronellol, however, were found to have iodine values of 175 and 187 respectively. It is worthy of note that, whilst artificial otto is considerably deodorised by iodine, the odour of the natural oil is not affected.

W. P. S.

Estimation of Methyl Alcohol in Formaldehyde. ROBERT GNEHM and FELIX KAUFLE (Zeit. angew. Chem., 1904, 17, 673—676).—Twenty-five c.c. of water are heated to boiling in a distilling flask and 90 grams of crystallised sodium sulphanilate are gradually added, and the boiling continued until all is dissolved. The contents are now rapidly cooled while stirring with a glass rod. To the crystalline mass is now added 20 c.c. of the formaldehyde to be tested, and, after closing the flask, the whole is left for 3 or 4 hours; $1\frac{1}{2}$ —2 hours is long enough if the flask is put into a water-bath at 35—40°. The formaldehyde has now entered into combination, whilst the methyl alcohol is unaffected and may be recovered by connecting the flask with a suitable condensing apparatus and collecting the first 35 c.c. which pass over. These are then made up to 50 c.c. and the amount of methyl alcohol is found from the sp. gr. of the solution at 15°. A sp. gr. table is given.

L. DE K.

Estimation of Alcohol in Wine. E. MARTIN (Rev. intern. Falsif., 1904, 17, 48—49).—Ten c.c. of the wine are diluted to a volume of 50 c.c. Of this solution, 10 c.c. are placed in a flask of 50 c.c. capacity and distilled, the distillate being collected in a second flask containing 25 c.c. of potassium dichromate solution and 10 c.c. of sulphuric acid. The dichromate solution contains 42.6087 grams of the pure dry salt per litre and 1 c.c. corresponds with 0.01 gram of alcohol. At the conclusion of the distillation, the excess of dichromate is titrated with ferrous ammonium sulphate solution in the usual manner.

W. P. S.

Volumetric Estimation of Sugar. LEOPOLD ROSENTHALER (Zeit. anal. Chem., 1904, 43, 282—285).—The products of the oxidation of dextrose and lævulose by alkaline copper solution are acids, and the amount of sugar oxidised can be estimated by the amount of alkali which these acids neutralise. The copper solution recommended is composed of 17.5 grams of crystallised copper sulphate, 75 grams of glycerol, 125 grams of sodium citrate, 100 grams of 15 per cent. sodium hydroxide solution, and water to 1 litre. The solution should be filtered after remaining for 3 or 4 days, or heating for a few hours on the water-bath, and then undergoes no further alteration on keeping. About 0.05 gram of sugar in 1 per cent. solution is mixed with a small excess (30 c.c.) of the copper solution, and boiled for 5 minutes. The precipitate is removed by a Gooch filter and washed with 150 c.c. of water. The filtrate is mixed with an excess of *N*-sulphuric acid, then nearly neutralised, boiled for 10 minutes, and exactly titrated with *N*-alkali and phenolphthalein. The original solution is titrated in the same manner: 1 c.c. of *N*-acid corresponds with 0.0225 gram of anhydrous dextrose or lævulose.

M. J. S.

Formaldehyde in Wine. F. MALLMANN (*Zeit. öffentl. Chem.*, 1904, 10, 165—166).—The author has recently met with a preservative powder for wine which was found to consist of formaldehyde and sodium chloride. It was sold under the name "Sterilisol."

With regard to the detection of formaldehyde in wine, it is pointed out that the phenylhydrazine reaction also gives a coloration with acetaldehyde.

W. P. S.

Estimation of Formaldehyde and its Polymerides. ADOLPHE SEYEWETZ and GIBELLO (*Bull. Soc. chim.*, 1904, [iii], 31, 691—694).—When a standard solution of sulphuric acid is added to a solution of sodium sulphite and trioxymethylene tinted with phenolphthalein, the quantity of acid necessary to effect decolorisation is proportional to the amount of trioxymethylene present. Lemme has suggested that the addition of sulphuric acid under these conditions results in the formation of sodium hydrogen sulphite, which is removed from the sphere of action by combination with the trioxymethylene. The authors have applied this reaction to the estimation of formaldehyde and its polymerides. Twenty c.c. of a 20 per cent. solution of sodium sulphite to which one drop of 0.2 per cent. solution of phenolphthalein in alcohol has been added is just decolorised by the addition of *N*-sulphuric acid. From 0.5 to 0.7 gram of trioxymethylene is then added, and the solution is again titrated with *N*-sulphuric acid until the pink colour disappears. This method gives results agreeing with those obtained by the processes of Legler (*Abstr.*, 1883, 1035) and Losekann (*Abstr.*, 1889, 1036), and is more easy to carry out.

T. A. H.

Estimation of Aldehydes in Wines and Spirits. L. MATHIEU (*Rev. intern. Falsif.*, 1904, 17, 43—45).—One hundred c.c. of wine are placed in a 120 c.c. flask, 1 gram of tartaric acid and 0.03 gram of sulphurous acid are added, and, after mixing, the flask and its contents are placed in the dark for 4 hours. The sulphurous acid may be added in the form of sodium hydrogen sulphite solution, 20 c.c. of which should contain 0.03 gram of sulphurous acid. At the end of 4 hours, the contents of the flask are transferred to a beaker, a few drops of starch solution are added, and then iodine solution until a blue coloration appears. Sufficient sodium arsenite solution is now added to destroy the excess of iodine and the combined sulphurous acid estimated by de Haas' method (*Abstr.*, 1902, ii, 582).

In the case of red wines, the starch indicator is used in the form of drops on a white tile. For estimating aldehydes in spirits, 2 grams of tartaric acid and 0.4 gram of sulphurous acid should be added.

The amount of barium sulphate obtained multiplied by 1.884 gives the weight of acetaldehyde present.

W. P. S.

Estimation of Volatile Acidity in Wines. LUCIEN ROBIN (*J. Pharm. Chim.*, 1904, [vi], 19, 531—533).—Water is boiled in a conical flask fitted with a safety funnel. The steam escapes through two separate delivery tubes and is passed through two receivers each containing 10 c.c. of a sample of wine to be tested. The whole is placed

on an iron stand covered partly with copper gauze, on which rests the steam-generating flask, and partly with a sheet of copper which supports the two receivers, the contents of which are also kept near the boiling point by means of the specially constructed burner.

After the current of steam has passed through for about 40 minutes, the remaining acidity is titrated as usual and the result deducted from the total acidity represents the volatile acidity. L. DE K.

Detection of Thiocyanic Acid in Saliva. EGIDIO POLLACCI (*Ann. Chim. anal.*, 1904, 9, 162).—The test is based on the partial reduction of mercurous chloride by potassium thiocyanate. In order to detect a thiocyanate in saliva, a little calomel is placed in a small capsule, 10–12 drops of the saliva are added, and the mixture is stirred with a glass rod; after a few minutes, a precipitate of metallic mercury will be noticed. The supernatant liquid contains mercuric thiocyanate, which develops a red coloration on adding ferric chloride. L. DE K.

Detection and Chlorimetric Estimation of Salicylic Acid. CARLO MONTANARI (*Gazzetta*, 1904, 34, i, 290–292).—Under the conditions used by Spica (*Abstr.*, 1895, ii, 426) in his method for determining salicylic acid, products other than picric acid are obtained, especially nitrosalicylic acids. The transformation into picric acid becomes complete, however, even with very minute quantities of salicylic acid, when sufficient nitric acid is taken to allow of boiling the liquid for several minutes. Only then can concordant results be obtained. T. H. P.

Composition of Milk. H. DROOP RICHMOND (*Analyst*, 1904, 29, 180–187).—The average composition of 15,313 samples of milk analysed during the year 1903 is given. The figures for the morning and evening milk for each month are given separately. The average percentage of fat (3.83) for the year was slightly higher than in 1902 (3.82) and, as usual, the poorest milk occurred in June, whilst the richest was found in October and November.

To ascertain whether the geological formation has any influence on the composition of milk, supplies from farms on four different formations were separately examined. It is, of course, doubtful whether the chief influence is not due to the surface soils, modified as they are by artificial manuring. The formations chosen comprised the new red sandstone, Oxford clay, upper green sand, and chalk. The only conclusion to be drawn from the results of the analyses is that the milk raised on the two cretaceous formations tends to be better in quality than the others; but the difference is not marked.

The author also discusses Storch's theory that the fat globules in milk are surrounded by a semi-solid membrane of mucoid substance, and considers that this assumption must be regarded as disproved. W. P. S.

Decrease in the Amount of Citric Acid in Milk on Heating. GUSTAV OBERMAIER (*Arch. Hygiene*, 1904, 50, 52–65).—The results

of the author's investigation show that the citric acid naturally present in milk diminishes in quantity when the latter is heated. For temperatures between 75° and 80°, the decrease is proportionately small, but when the milk is boiled or heated in an autoclave at 120°, the decrease in the amount of citric acid is very marked, in some cases reaching 30 per cent. of the total quantity. Scheibe's method (Abstr., 1891, i, 1276) was used for the estimation of the citric acid.

W. P. S.

Estimation of Fat in Cheese. MORITZ SIEGFELD (*Milch-Zeit.*, 1904, 33, 289—292).—The various methods recommended for this estimation are compared with one another. The processes investigated included direct extraction of the cheese, after grinding it up with sand and drying, with ether or light petroleum; dissolving the cheese in hydrochloric acid before extracting; Gottlieb's ammonia-alcohol-ether process, and finally that of Gerber. The results obtained by the different methods agreed well with each other. In the case of cheese made from skimmed milk, direct extraction gave slightly lower results, and in using the Gottlieb process incorrect amounts of fat were sometimes obtained owing to incomplete solution of the casein. The hydrochloric acid method is considered the best for general use, but Gerber's method is also trustworthy provided that the lower meniscus is taken in reading off the volume of the fat.

W. P. S.

Estimation of Fat and Sugar in Molasses Foods. D. J. HISSINK (*Landw. Versuchs-Stat.*, 1904, 60, 125—134).—Fat was estimated (1) by extracting the dried substance with ether; (2) by extracting after washing out with water; and (3) by Berntrup's method (Abstr., 1902, ii, 366), using 100 c.c. of 10 per cent. hydrochloric acid and 50 c.c. of water with 5 grams of the dried substance. Berntrup's method gave the highest results and the first method the lowest.

The following method was employed for estimating the sugar. The molasses (25 grams) is agitated with 400 c.c. of water in a half-litre flask for half an hour, the whole made up to 500 c.c., and left for half an hour. Two hundred c.c. are then drawn off into a quarter-litre flask and the estimation continued according to the Dutch method. The solution is treated successively with lead acetate and sodium carbonate, being filtered after each addition, neutralised with hydrochloric acid, and inverted by heating on boiling water-bath for 30 minutes with 30 c.c. of *N*/10 hydrochloric acid.

N. H. J. M.

Estimation of Morphine in Opium. PHILIP SCHIDROWITZ (*Analyst*, 1904, 29, 144—148).—Six grams of opium are thoroughly mixed into a paste with 6 c.c. of water and then transferred to a counterpoised 100 c.c. Erlenmeyer flask. Water is then added to bring the weight of the contents up to 54 grams. The flask, after corking, is shaken for 1 hour, the contents being then poured on a filter and the filtrate collected in a second counterpoised flask. Exactly 42 grams of filtrate are collected, 2 grams of a 50 per cent. sodium salicylate solution are added, the mixture is shaken for half a minute, and filtered. To 36 grams of the filtrate, 15 c.c. of ether are

added, and also 5.2 c.c. of ammonia solution, prepared by mixing 17 grams of ammonia of sp. gr. 0.960 with 83 grams of water. The whole is then shaken for 10 minutes and placed aside for 24 hours. As much as possible of the ether is now poured on to a filter, 15 c.c. of fresh ether are added to the flask, and, after well shaking, also passed through the filter together with the whole of the liquid contents of the flask. The crystals remaining in the flask are washed with 3 successive quantities of 5 c.c. of water saturated with ether, about 3 c.c. being used to rinse the flask and 2 c.c. run directly on the filter. The latter and its contents are then pressed between blotting-paper, the greater part of the crystals are returned to the flask, and both filter and flask dried at a temperature of 55°. Any crystals remaining on the filter are then readily transferred to the flask. The crystals are now dissolved in 25 c.c. of *N*/10 sulphuric acid, the solution is diluted to 50 c.c. with water, and the excess of acid titrated back, using methyl-orange as indicator. The percentage of morphine is calculated from the formula: $x \times 0.7575 + \frac{1}{3} (x \times 0.7575) = \text{morphine per cent.}$, where x equals the number of c.c. of *N*/10 acid employed.

W. P. S.

Estimation of Vegetable Proteids. L. BEULAYGUE (*Compt. rend.*, 1904, 138, 701—703).—The total amount of proteids is estimated by heating the dry powdered substance (4 grams) for 10 minutes with 100 c.c. of water at the boiling point. Alum (0.5 gram) and glacial acetic acid (4 c.c.) are then added and the heating continued for 5 minutes longer. The undissolved substance is washed and dried, and the nitrogen determined.

The proteids insoluble in water are estimated in a similar manner, omitting treatment with alum and acetic acid, and the amount of soluble proteids is obtained by deducting the result from the total proteids.

The total indigestible proteid (including nucleins and lecithins) is estimated by digesting the substance (4 grams) with pepsin and hydrochloric acid at 37—40° for 12—15 hours. The undissolved nitrogen is estimated in the usual manner. The nucleins alone can be estimated in the undissolved residue obtained by macerating the dried substance (after digestion) for 24 hours with 50 c.c. of a mixture of ether and alcohol (equal vols.).

N. H. J. M.

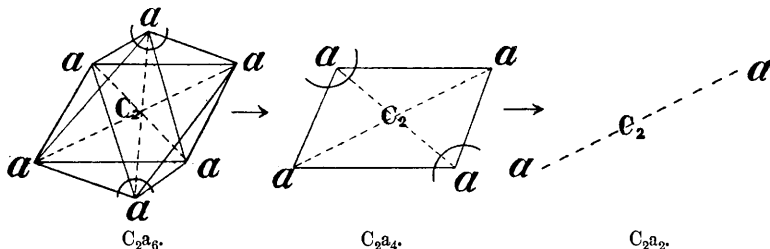
Polariscopic Estimation of Gliadin in Wheat-Flour. HARRY SNYDER (*J. Amer. Chem. Soc.*, 1904, 26, 263—266).—15.97 grams of the sample of flour are treated with 100 c.c. of 70 per cent. alcohol, and the whole is gently shaken at intervals of half an hour for two hours; too violent shaking is apt to produce a turbid filtrate. After further contact with the alcohol for 12 to 18 hours, the liquid is polarised at 20° in the 22 cm. tube. The reading expressed in sugar multiplied by 0.2 approximates very closely to the percentage of gliadin-nitrogen in the sample.

L. DE K.

General and Physical Chemistry.

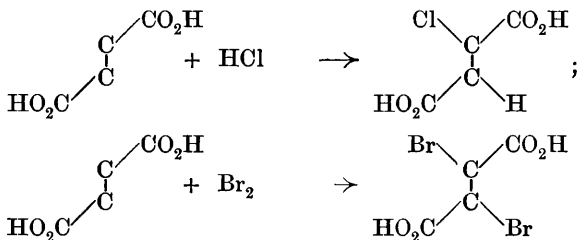
Stereochemistry of Carbon Compounds, especially of Unsaturated Systems. PAUL PFEIFFER (*Zeit. physikal. Chem.*, 1904, 48, 40—62).—The consequences of the van't Hoff-Wislicenus theory, dealing with the isomerism of maleic and fumaric acids and of ethylenic substances in general, are not always in harmony with the experimental facts (compare Michael, *Abstr.*, 1893, i, 145). Thus, in conflict with the theory, addition of hydrogen chloride, hydrogen bromide, or bromine to acetylenedicarboxylic acid produces principally substances of the fumaroid form, whilst, conversely, compounds of the fumaric acid type pass more readily than those of the maleic acid type into acetylene derivatives.

To adapt the theory to the facts, the author gives up the idea of double and triple linkings, and also the conception of valency as a definitely directed single force (compare Lossen, *Abstr.*, 1888, 218). He further represents the compound C_2a_6 by a regular octahedron with the C_2 complex at the centre. The compound C_2a_4 is then derived from C_2a_6 by the removal of two a groups at opposite corners of the octahedron, a plane four-sided figure being left. C_2a_2 is then derived from C_2a_4 by the removal of two diametrically opposite a groups. These relationships are represented diagrammatically thus :



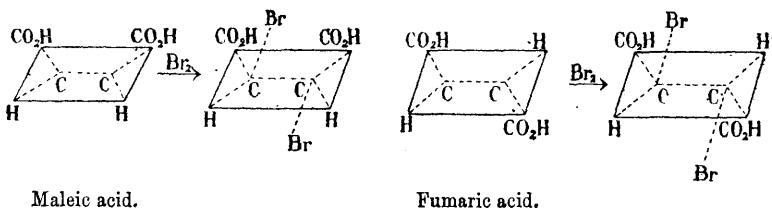
There is a marked analogy between the space formulæ here suggested for the C_2 substances and those developed by Werner for inorganic molecular compounds (compare Werner, *Abstr.*, 1893, ii, 379).

When substances of the acetylene type are regarded as essentially *trans*-forms in the way shown above, then the production of chloro- and dibromo-fumaric acids by addition of hydrogen chloride and bromine respectively to acetylenedicarboxylic acid becomes intelligible, thus :



Similarly, the more ready conversion of the halogen fumaric acids into acetylenedicarboxylic acid is satisfactorily accounted for, as is also the fact that from the silver salt of bromomaleic acid carbon dioxide and silver bromide are eliminated more readily than from the silver salt of bromofumaric acid.

The author further shows that the conversion of maleic acid into the dibromosuccinic acid (m. p. 160°), which corresponds with racemic acid, and of fumaric acid into the dibromosuccinic acid (m. p. 255°), which corresponds with mesotartaric acid, is to be expected from the formulæ given above, thus:

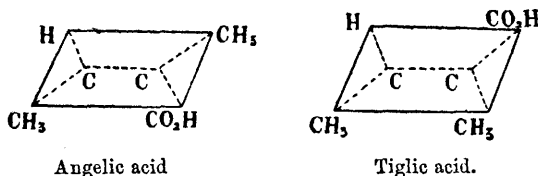


An adequate interpretation of the oxidation of maleic and fumaric acids in terms of the author's system is more difficult, but can be given on the supposition that an oxide is first produced, and that the dihydroxysuccinic acids are secondarily formed by the action of water.

Extending these considerations to other ethylenic compounds which do not give anhydrides, and in regard to which the important point is their relationship to the corresponding compounds of the acetylene and ethane types, the author arrives at a number of formulæ which differ from those of Wislicenus. Thus, of the following pairs of compounds, the first-mentioned is to be regarded as a *trans*-form, the second as a *cis*-form:

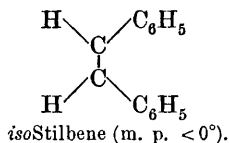
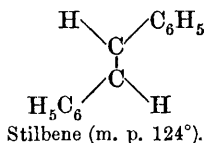
Crotonic acid (m. p. 72°); *isocrotonic* acid (m. p. 15°); α -chloro-crotonic acid (m. p. 97°); α -chloro*isocrotonic* acid (m. p. 66°); β -chloro-crotonic acid (m. p. 94°); β -chloro*isocrotonic* acid (m. p. 61°); α -bromo-crotonic acid (m. p. 106°); α -bromo*isocrotonic* acid (m. p. 92°); dibromocrotonic acid (m. p. 95°); dibromo*isocrotonic* acid (m. p. 120°) (compare Bruni and Gorni, Abstr., 1899, ii, 731).

Of the two monobromobutylenes, the one boiling at 93 – 94° must be the *cis*-compound, because potassium hydroxide converts it only with difficulty into crotonylene; the one boiling at 87 – 88° is easily decomposed by potassium hydroxide, and is therefore the *trans*-form. Hence angelic and tiglic acids must have the configurations:



Of the two butylenes, the one boiling at 2.5° is the *cis*-form; the one boiling at 1.5° is the *trans*-form.

Of the two monobrostilbenes, the one melting at 31° must be the *trans*-form, since hydrogen bromide is more easily removed from it than from bromostilbene (m. p. 19°). Hence the configurations of the two stilbenes are:



J. C. P.

Configuration of Maleic and Fumaric Stereoisomerides and of the Corresponding Acetylene Compounds. GIUSEPPE BRUNI (*Atti R. Accad. Lincei*, 1904, [v], 13, i, 626—632).—The author discusses the views of Pfeiffer (preceding abstract) in conjunction with the work published during the last few years by himself, Garelli and Calzolari, Boeris, and Mascarelli, and gives the following tabular *résumé* of the results obtained:

| Saturated compounds. | Compounds not forming solid solutions with saturated compounds. | Compounds forming solid solutions with saturated compounds. | |
|---|---|--|---------------------------------------|
| | Ethylenic compounds. | Ethylenic compounds. | Acetylenic compounds. |
| Ethyl dimethylsuccinate (19°) Butyric acid (4°) | Ethyl dimethylmaleate (liq.) <i>iso</i> Crotonic acid (liq.) | Ethyl dimethylfumarate (102°) Crotonic acid (72°) | Ethyl dimethylacetylenedicarboxylate. |
| Phenylpropionic acid (48°) Dibenzyl (52°) Dimethyldibenzyl (82°) | Allocinnamic acid (69°) <i>iso</i> Stilbene (liq.) — | Cinnamic acid (133°) Stilbene (124°) <i>pp</i> -Dimethylstilbene (177°) | Phenylpropionic acid Telane — |

The numbers in brackets in the above table represent melting points.

The general conclusions drawn by the author are that: (1) all the compounds in the third column of the table possess configurations corresponding with those of the respective saturated compounds (the fumaroid structure), and with this their physical and chemical properties are in accord, for (a) they all have melting points higher than those of their isomerides given in the second column and higher by 70 — 90° than those of the corresponding saturated compounds, (b) they are all less soluble than their isomerides, and (c) they are all more stable than their isomerides, which are transformed into them with

ease, for example, by the action either of traces of iodine or of light.
 (2) The compounds in the second column have a maleinoid configuration.
 T. H. P.

Fluorescence. V. The Benzene Ring-system. HUGO KAUFFMANN and ALFRED BEISSWENGER (*Ber.*, 1904, 37, 2612—2617).—The following table shows how the fluorescence and colour of 3-aminophthalimide varies with the solvent, but is not directly related to the dispersion (Kundt's rule):

| | Fluorescence. | Colour. | Dispersion of Solvent. |
|--------------------------------|---------------|-------------|------------------------|
| Water | green | yellow | 326 |
| Acetic acid | ↓ | | 374 |
| Alcohol (absolute) | blue-green | ↓ | 330 |
| <i>iso</i> Butyl alcohol | | | 378 |
| Pyridine | ↓ | | — |
| Amylene | ↓ | ↓ | 461 |
| Chloroform | blue | pale yellow | — |
| Acetone | ↓ | | 388 |
| Anisole | ↓ | | 1086 |
| Thiophen | blue-violet | ↓ | 1086 |
| Ether (absolute) | ↓ | ↓ | 351 |
| Benzene | violet | colourless | 1056 |

This change is characteristic of all fluorescent, and also appears in the non-fluorescent amines, and is not hindered by substituting alkyl or aryl groups. As the molecular weight is normal even in associating solvents, the conclusion is drawn that the change of colour is not due to reversible isomeric or polymeric change, but rather to the distortion of the benzene ring-system.
 T. M. L.

Origin of Radium. HERBERT N. MCCOY (*Ber.*, 1904, 37, 2641—2656. Compare Rutherford and Soddy, *Abstr.*, 1903, ii, 463).—Radioactivity accompanies or is caused by decomposition of the active substance. The apparent permanency of radium must be due to the extreme slowness of its decomposition, and its present existence can be explained only by supposing it to be formed by the decomposition of another substance, to which it must stand in the same relation as thorium X to thorium. The fact that radium is found in many uranium minerals suggests that these elements are genetically related. If radium is a decomposition product of uranium, then all uranium minerals should contain radium in a constant proportion to the uranium present. In agreement with this, the activity constant K , which is the radioactivity of a given mass divided by the percentage of uranium present, for pure uranium salts is 3.86, whilst for twelve samples of uranium minerals, K is found to be 18.9—24.7 (mean 22.1). The radioactivity of a uranium mineral is 5.7 times that of the pure uranium salt obtained from it. As the activity of radium is 1.5×10^6 greater than that of uranium, it follows that one part by weight of radium is contained in a mineral containing 300,000 of uranium.

The author concludes that radium is a member of the following series of successive decomposition products of uranium: $U \rightarrow UX \rightarrow Ra \rightarrow Ra\text{ Em} \rightarrow EmX \rightarrow He$.
G. Y.

Properties and Changes of Radium Emanation. Sir WILLIAM RAMSAY (*Compt. rend.*, 1904, 138, 1388—1394).—The radium emanation was collected from a solution of 70 mg. of radium bromide in water, which yields also electrolytic gases containing an excess of hydrogen; the gas was exploded and the residual hydrogen and radium emanation dried, transferred to a small glass vessel, and cooled in liquid air; this caused the radium emanation to condense, and the tube became so luminous that the face of a watch could be clearly seen by its light; the hydrogen was removed by means of a mercury pump until the escaping bubbles of gas were slightly luminous, due to the appreciable vapour pressure of the radium emanation even at the temperature of liquid air. After the removal of the hydrogen, the radium emanation was rendered gaseous and a series of measurements of the volume and pressure were made; the results showed that the emanation is a true gas obeying the Boyle-Mariotte law, the mean value of the product VP being 19.3, and corresponding to a volume of 0.0254 cm. at normal pressure. The volume of the radium emanation gradually diminished and the luminosity faded, until at the end of a month all luminosity had disappeared; on gently warming the tube, a quantity of gas four times the volume of the original emanation was obtained, and this gas gave the spectrum of helium.

The remainder of the paper is a summary of the work described in the following abstract.
M. A. W.

Spectrum of the Radium Emanation. Sir WILLIAM RAMSAY and J. NORMAN COLLIE (*Proc. Roy. Soc.*, 1904, 73, 470—476).—The spectrum of the emanation from radium bromide has been mapped with as great exactness as possible, and the observed lines are recorded in the paper. A considerable difficulty, however, arises, in that, although the spectrum of the emanation is very brilliant at first, it is in a few minutes completely masked by the hydrogen spectrum. The origin of this hydrogen is matter of speculation: it may have come from the electrodes; the emanation may not have been completely dried, or hydrogen may be one of the disintegration products of the emanation as well as helium.

The authors consider that sufficient evidence has now been accumulated showing that the emanation from radium is an element, although a transient one. It is a gas, and follows Boyle's law; it resembles the gases of the argon series in its indifference to chemical reagents; its molecular weight has been found to be nearly 200. For this element, the authors suggest the name "exradio."
J. C. P.

Penetrating Radium Rays. J. A. McCLELLAND (*Phil. Mag.*, 1904, [vi], 8, 67—77).—The author has endeavoured to discover whether the γ -rays carry any positive or negative charge, without, however, arriving at any definite result (compare Paschen, this vol., ii, 461). As shown by Rutherford, the absorption of γ -rays by different substances is roughly proportional to their density, but for denser sub-

stances the ratio of the coefficient of absorption to the density is greater than the normal value, being twice as great for lead as for water. Further experiments made by the author show that when the rays have passed through some thickness of the denser substances, the coefficient of absorption is diminished, so that the law that the coefficient of absorption is proportional to the density is then followed very closely.

J. C. P.

Origin of the Energy Emitted by Radioactive Substances. C. BONACINI (*Atti R. Accad. Lincei*, 1904, [v], 13, i, 466—473).—No experiments have yet been made to determine whether the source of the energy of radioactive substances is intramolecular change or absorption of an unknown form of energy coming from outside. In order to obtain information on this point, the author has carried out the following experiment. A radioactive substance was enclosed in a covering opaque to radioactive rays, together with a substance for indicating its action, for instance, one which changes colour under the influence of the rays emitted. In a second similar arrangement, the opaque screen was surrounded with radioactive material. If the source of the energy of radioactive matter is external, the enclosed substance should, after some time, be less active in the second case than in the first. With the but slightly active material at the author's disposal, no such difference could be detected.

T. H. P.

Testing of Minerals for Radioactivity. FELIX PISANI (*Chem. Centr.*, 1904, i, 1433; from *Bull. Soc. franç. Min.*, 27, 58—63).—In order to test minerals for radioactivity the specimens are placed above a small triangular hole cut in a sheet of metal which is laid on the sensitive plate. After remaining from 1 to 24 hours, the images are developed and compared. From the results obtained, it appears that all the radioactive minerals, with the exception of the coloured fluorspars, and other minerals which contain organic pigments, are characterised by containing either oxide of uranium or of thorium or both. It is doubtful, however, whether the 1 to 3 per cent. of these oxides which is present in some of the minerals is sufficient to wholly account for their great radioactivity.

E. W. W.

Pyroradioactivity. THOMAS TOMMASINA (*Arch. Sci. phys. nat.*, 1904, [iv], 17, 589—596).—Metals, when heated by an electric current, become radioactive and are capable of discharging electrosopes, &c. All the metals emit rays capable of discharging either electrification, but the difference between the two actions is generally very great. Iron, copper, and platinum produce a more rapid discharge of negative electrification, whilst for silver and zinc the opposite is the case. If the current increases, however, the difference between the two effects tends to disappear, and at bright incandescence the metal discharges both electrifications almost equally. The radioactivity of a metallic thread heated to redness by a current diminishes along an asymptotic curve, but its power is regained by rest for some time, or by light friction. When the

radioactivity has become weak, it continues for some time after the heating of the current, but is lost if the wire is struck. A mantle of glass or aluminium surrounding the wire also becomes radioactive. Three types of emissions exist: the α , easily arrested by screens, the β , more penetrative, and the γ , which discharge either electrification, induce fluorescence, &c. They are, however, less penetrative than the γ -rays of radium. L. M. J.

Rate of Decay of Thorium Emanation. C. LE ROSSIGNOL and C. T. GIMINGHAM (*Phil. Mag.*, 1904, [vi], 8, 107—110).—The authors find that the time required for thorium emanation to decay to half-value is 51 seconds, instead of 60 seconds, as found by Rutherford (*Abstr.*, 1900, ii, 351). J. C. P.

The Property a Large Number of Substances Possess of Projecting Spontaneously and Continuously a Ponderable Emanation. R. BLONDLOT (*Compt. rend.*, 1904, 138, 1473—1476).—The author describes a series of experiments in which a screen of phosphorescent calcium sulphide was found to glow more brightly when a silver coin was placed near it. The relative positions of the coin and screen for points of maximum brightness indicate that the coin emits a ponderable emanation normal to its surface and with a small velocity, the path of which is not parabolic, but a curve with a vertical asymptote; when this emanation strikes the screen, it causes an increase in the luminosity of the calcium sulphide. Similar results were obtained with copper, zinc, lead, or moist cardboard instead of the silver coin, but gold, platinum, glass, or dry cardboard were inactive in this respect. The emanation can penetrate a sheet of paper or cardboard, or even a 2 cm. plank, but it is stopped completely by a sheet of glass. M. A. W.

A Phenomenon analogous to Phosphorescence produced by n -Rays. E. BICHAT (*Compt. rend.*, 1904, 138, 1316—1318).—Blondlot has shown (compare *Compt. rend.*, 1903, 137, 729) that certain substances are capable of absorbing n -rays and emitting them after the removal of the original source of the rays; on heating such a substance, there is a temporary increase in the number of the secondary rays, followed by a rapid disappearance of the same; this phenomenon is analogous to the behaviour of ordinary phosphorescent substances when heated. An examination of the indices of refraction of these secondary rays, using Blondlot's method (compare *Compt. rend.*, 1904, 138, 125), shows that they conform to Stokes' law, the wave-length of the secondary ray being longer than that of the primary. Copper, zinc, and glass have the property of absorbing n -rays, whilst platinum, silver, or aluminium have not, and there is no relation between this property of emitting secondary rays and transparency to n -rays, for platinum is opaque, whilst silver and aluminium are transparent. M. A. W.

Emission of n - and n_1 -Rays by Crystalline Substances. E. BICHAT (*Compt. rend.*, 1904, 138, 1396—1397).—Positive crystals such as quartz, apophyllite, brucite, cassiterite, or zircon emit n -rays in the direction of the axis, and n_1 -rays in a direction at right angles to this, whilst negative crystals, such as iceland spar, corundum, emerald, idocrase, or oligiste, do just the reverse, emitting n_1 -rays in the direction of the axis, and n -rays in a normal direction. A thick sheet of ordinary glue emits n_1 -rays in a direction normal to the plane and n -rays in a direction at right angles to it; this is in keeping with Bertin's observation that a pile of thin sheets of gelatin behaves like a uniaxial positive crystal (compare *Ann. Chim. Phys.*, 1878, [v], 15, 129). Tourmaline behaves in this respect as a normal negative crystal, but if it be warmed it becomes pyroelectric, and the positively charged pole of the crystal causes an increase in the luminosity of a phosphorescent screen, whilst the negatively charged pole causes a diminution in the same. M. A. W.

Use of n -Rays in Chemistry. ALBERT COLSON (*Compt. rend.*, 1904, 138, 1423—1425. Compare this vol., ii, 377).—When barium hydroxide solution is added to zinc sulphate solution, the whole of the zinc is precipitated in the form of the basic salt, $\text{SO}_4(\text{Zn}\cdot\text{O}\cdot\text{ZnOH})_2$, by three-fourths of the quantity of the base equivalent to the metallic salt, and the heat development accompanying this reaction is 17.8 Cal.; if, however, the zinc sulphate solution be added to the barium hydroxide solution, zinc hydroxide is formed accompanied by an emission of n -rays and a thermal change of 13.4 Cal. The results are analogous to those obtained with zinc sulphate and potassium hydroxide (this vol., ii, 377), and similar results were obtained with copper sulphate and barium hydroxide. M. A. W.

Action of Sources of n -Rays on Pure Water. JULIEN MEYER (*Compt. rend.*, 1904, 138, 1491—1492).—When water is subjected to the action of a source of n -rays, it becomes itself a source of n_1 -rays; this is shown by the following experiments: (1) when a file is placed below a crystallising dish containing water, above the surface of which is a screen of calcium sulphide, the phosphorescence of the screen diminishes as the file approaches the dish, whereas the ordinary effect of the n -rays is produced if the dish contains no water; (2) when a file, or any other source of n -rays, is plunged into pure water contained in a glass vessel, the phosphorescence of a calcium sulphide screen held near to the vessel is diminished, showing that the water has become a source of n_1 -rays; (3) a vessel of water containing a frog, or the green parts of a plant, is also a source of n_1 -rays. The addition of a few drops of chloroform to the water destroys its power of emitting n_1 -rays, and the source of the n -rays then exerts its characteristic action on the phosphorescent screen. A similar series of experiments in which a source of n_1 -rays was used, instead of a source of n -rays, showed that water is transparent to these rays, and the addition of chloroform to the water did not modify in any way the normal action of the n_1 -rays. M. A. W.

Influence of Pressure on the E.M.F. of Gas Electrodes. THEODOR WULF (*Zeit. physikal. Chem.*, 1904, 48, 87—96).—The decomposition point observed galvanometrically is the point at which the discharged gas ions dissolve appreciably in metal and electrolyte. The point at which bubbles are visibly formed is reached when the gas is evolved from a saturated solution. The latter point is dependent, the former point is not dependent, on the pressure, as might be expected from the fact that the evolution of gaseous bubbles means a large increase of volume, whilst the process of solution in metal or electrolyte does not involve any such great volume change. The two points nearly coincide when the gas in question is but slightly soluble, as, for instance, hydrogen and oxygen at the ordinary pressure. They are quite distinct, however, in the case of a soluble gas such as chlorine.

Helmholtz's formula for the variation of the *E.M.F.* of the hydrogen electrode with pressure has been verified for the range 1—1000 atmospheres.
J. C. P.

Behaviour of Glycogen under the Influence of the Electric Current. MADAME Z. GATIN-GRUZEWSKA (*Pflüger's Archiv*, 1904, 103, 287—288).—Glycogen behaves like other colloids and wanders to the anode.
W. D. H.

Liquefied Hydrides of Phosphorus, Sulphur, and the Halogens as Conducting Solvents. I. DOUGLAS MCINTOSH and BERTRAM D. STEELE (*Proc. Roy. Soc.*, 1904, 73, 450—453).—As a preliminary to the main investigation, a number of physical constants of the above-mentioned solvents have been measured. The vapour pressure curves have been determined by the method of Travers, Senter, and Jaquerod, and from these curves the following melting and boiling points have been read: hydrogen chloride, b. p. -82.9° ; hydrogen bromide, m. p. -86° , b. p. -68.7° ; hydrogen iodide, m. p. -50.8° , b. p. -35.7° ; hydrogen sulphide, b. p. -60.1° ; hydrogen phosphide, b. p. -86.2° . The densities of the liquids were determined over a wide temperature range, and the values at the boiling point for hydrogen chloride, bromide, iodide, sulphide, and phosphide are respectively 1.195, 2.157, 2.799, 0.964, 0.744. A study of the molecular surface energy shows that of the substances examined the bromide, iodide, and sulphide occur as simple molecules, whilst the chloride and phosphide are more or less associated. The viscosities also have been measured, and the following temperature-coefficients of viscosity have been obtained: hydrogen chloride, 0.88; hydrogen bromide, 0.57; hydrogen iodide, 0.70; hydrogen sulphide, 1.10. In the preliminary investigation, the organic ammonium salts were found to dissolve readily to conducting solutions, the conductivity of which increased enormously with increasing concentration, in sharp contrast to the behaviour of aqueous solutions (see also following abstract). No metallic salts appeared to dissolve; at any rate, none were found to conduct the current. Hydrogen chloride and bromide dissolve readily in liquid hydrogen sulphide, but give non-conducting solutions.

J. C. P.

Liquefied Hydrides of Phosphorus, Sulphur, and the Halogens as Conducting Solvents. II. EBENEZER H. ARCHIBALD and DOUGLAS MCINTOSH (*Proc. Roy. Soc.*, 1904, 73, 454—455. Compare preceding abstract).—In hydrogen chloride, bromide, iodide, and sulphide, many organic substances are readily soluble, such as amine salts, acid amides, certain alkaloids, alcohols, ethers, ketones, phenols, and some organic acids and esters. In every case where a conducting solution is formed, the dissolved substance contains an element (nitrogen or oxygen) the valency of which may be increased. In every one of the large number of solutions examined, the molecular conductivity was found to increase enormously with increasing concentration. The solutions rarely conduct better than $N/25$ KCl. Many temperature-coefficients have been determined, and these are found to be positive in the majority of cases. All the experiments go to indicate that the current is carried by the dissolved organic substance, not by the hydride. Discussion of the results is postponed until the molecular weights of the dissolved substances and the transport numbers have been determined.
J. C. P.

Anodic Behaviour of Copper and Aluminium. FRANZ FISCHER (*Zeit. physikal. Chem.*, 1904, 48, 177—219. Compare Abstr., 1903, ii, 587).—Details are given of work already described in outline (*loc. cit.*).
J. C. P.

Electrolysis of Alkali Chlorides. II. A. TARDY and PHILIPPE A. GUYE (*J. Chim. phys.*, 1904, 2, 79—123. Compare this vol., ii, 29).—The present paper treats of the function of the diaphragm during electrolysis. The diaphragm is the seat of four principal phenomena: (1) physical diffusion of the alkali from the cathode to the anode liquid, (2) migration of hydroxyl ions, (3) electrical endosmosis by which the anode liquid traverses the diaphragm, (4) flow of liquid from cathode to anode consequent on alteration of level due to 3. These effects are separately considered; the last is completely eliminated when the cathode solution is continually replenished and kept at a constant level. Characteristic constants for the different effects may be calculated from knowledge of the porosity and permeability of the diaphragm, and results of measurements with different diaphragms are given. In order to obtain the maximum yield of alkali, it is necessary to keep the levels of anode and cathode liquids equal and to employ a current density of sufficient magnitude to cause the endosmotic current to nullify that in the opposite sense due to diffusion. The latter may be done by altering the current for a given diaphragm or by choosing the latter with a permeability suited to the current employed.
L. M. J.

Some Considerations in Support of the Theory of "Mobile Ions." ALBERT REYCHLER (*J. Chim. phys.*, 1904, 2, 307—320).—The following views are put forward by the author. When a salt dissolves in water, it forms with some of the simple molecules of water (present in but small numbers) saline systems composed of equivalent quantities of acid and base; this reaction, being reversible, may be

represented thus: $MX + 1/n(H_2O)_n \rightleftharpoons MOH + HX$, so that a limiting value of the dissociation is reached. The constitutive parts of these saline systems are osmotically active, and hence the dissociation may be obtained from ebullioscopic or cryoscopic measurements. The conductivity is due to the reversibility, the equilibrium being dynamic, not static, so that under the directive influence of the electric tension

the systems become $\dots + (\overset{+}{M}\overset{-}{X} + HOH) + (\overset{+}{M}\overset{-}{X} + HOH) + \dots \rightleftharpoons \dots \overset{+}{M} + (\overset{-}{X}H + \overset{+}{M}OH) + (\overset{-}{X}H + HO \dots$, and hence separation of the ions M and X ensues. The conductivity is hence given by expression $\mu_v = x(u+v)$. The theory also explains the approximate

constancy of the heats of neutralisation, thus: $(\overset{+}{M}OH + \overset{-}{H}OH) + (\overset{-}{X}H + \overset{+}{M}OH) = (\overset{+}{M}OH + \overset{-}{X}H) + 2/n(H_2O)_n$, the heat developed being due to the formation of polymerised from simple water molecules. In the ordinary dissociation theory, it has to be assumed that the separation of the ions of a compound develops heat, a contradiction of thermal ideas. The author points out that the theory also does not necessitate the attributing of incomprehensible properties to the free ions, and explains equally well the catalytic decomposition of sucrose, methyl acetate, &c., by weak acids. In reply to sundry objections, it is

stated that the electromotive force expression $E = K\left(\log \frac{P}{p} - \log \frac{P'}{p'}\right)$ is given equally well by this theory if P and P' are understood to measure the tendency of the metals to form oxides saturated by acid, and p, p' are attributed to the molecules $Zn(OH)_2$, &c., in the saline systems at the electrodes.

L. M. J.

Ionic Reactions in Organic Chemistry. WALTHER LÖB (*Zeit. Elektrochem.*, 1904, 10, 367—368).—A claim for priority. T. E.

Combination of a Solvent with the Ions. J. LIVINGSTON R. MORGAN and C. W. KANOLT (*J. Amer. Chem. Soc.*, 1904, 26, 635—637). When a solution of silver nitrate and pyridine is submitted to electrolysis, a loss of pyridine occurs at the anode, and a corresponding gain at the cathode. Preliminary experiments with copper nitrate and water dissolved in alcohol indicated that in this case the quantity of water decreases at the anode and increases at the cathode. It is therefore concluded that when a substance undergoes ionisation on passing into solution, one or both of the ions form complex ions with a certain amount of the solvent.

By applying the law of mass action to such cases, the following results are obtained. When complex ions are formed from the simple ions but neither condenses, the equilibrium is in accordance with Ostwald's dilution formula. If two ions of one kind combine with the solvent to form one complex ion, that is, one ion condenses whilst the other does not, or if both ions condense, the equilibrium is expressed by van't Hoff's form of Rudolphi's dilution formula.

E. G.

Determination of the Concentration of the Hydrogen Ions in a Solution by means of Indicators. EDUARD SALM (*Zeit. Elektrochem.*, 1904, 10, 341—346).—Friedenthal (this vol., ii, 288) determined the concentration of the hydrogen ions in a series of standard solutions by means of their electrolytic conductivity. The author has redetermined these concentrations more accurately by means of concentration cells with hydrogen electrodes. The following table contains the results, the concentrations being given in gram equivalents per litre :

| Concentration of solution. | Concentration of H ions. | Concentration of solution. | Concentration of H ions. |
|--|----------------------------|----------------------------|----------------------------|
| 0·001 <i>N</i> HCl | $1\cdot11 \times 10^{-3}$ | 0·001 <i>N</i> KOH | $2\cdot6 \times 10^{-11}$ |
| 0·0001 <i>N</i> HCl | $0\cdot996 \times 10^{-4}$ | 0·0102 <i>N</i> KOH | $1\cdot3 \times 10^{-12}$ |
| 0·1 <i>N</i> NaH ₂ PO ₄ (solution <i>a</i>) | $3\cdot3 \times 10^{-5}$ | 0·104 <i>N</i> KOH | $1\cdot29 \times 10^{-13}$ |
| 2 c.c. sol. <i>b</i> + 8 c.c. sol. <i>a</i> | $1\cdot5 \times 10^{-6}$ | 1·38 <i>N</i> KOH | $1\cdot02 \times 10^{-14}$ |
| 4 " " + 6 " " " | $4\cdot9 \times 10^{-7}$ | 3·8 <i>N</i> KOH | $3\cdot1 \times 10^{-15}$ |
| 6 " " + 4 " " " | $1\cdot9 \times 10^{-7}$ | | |
| 8 " " + 2 " " " | $6\cdot5 \times 10^{-8}$ | | |
| 0·1 <i>N</i> Na ₂ HPO ₄ (solution <i>b</i>) | $1\cdot3 \times 10^{-9}$ | | |

The most strongly acid solutions could not be used, because the hydrogen carried away hydrogen chloride with it and so diminished the concentration. Very dilute solutions of acids or alkalis are not suitable owing to the large influence of the variable small quantities of impurity in even the purest water (see also Salessky and Fels, this vol., ii, 319—320). A solution containing 2×10^{-10} gr. eq. H ions per litre is prepared by diluting 60 c.c. *N*/100 KOH with *N*/10 NaCl to 1 litre. In addition to the indicators mentioned by Friedenthal, alizarin-green changes from lilac to flesh-pink between 2*N* and *NH*⁺, from brownish-yellow to green between 1×10^{-13} and 1×10^{-14} *NH*⁺, and from flesh-pink to brownish-yellow between 1×10^{-7} and 1×10^{-9} *NH*⁺. Alizarin changes from yellow to orange between 1×10^{-5} and 1×10^{-6} *NH*⁺, from orange to red between 1×10^{-7} and 1×10^{-10} *NH*⁺, and from red to a violet precipitate between 1×10^{-13} and 1×10^{-14} *NH*⁺. T. E.

Thermal Ionisation of Salt Vapours. GEORGES MOREAU (*Compt. rend.*, 1904, 138, 1268—1269).—A current of air which has been passed through an aqueous solution of the salt under investigation is then conducted through a porcelain tube heated at 1000°, in which its electrical conductivity is measured. For a solution of given concentration, the observed current is at first proportional to the difference of potential, but approximates to a limiting value as the voltage increases. For very dilute solutions of the same salt, this maximum current is proportional to the concentration, but tends to a limit as the concentration is increased. Of the salts examined, those of potassium are the best conductors, and the chloride, bromide, iodide, and nitrate conduct three or four times as well as other potassium salts. The salt vapours in these experiments are ionised, but the phenomena differ considerably from those observed in flames containing salt vapours (Abstr., 1903, i, 600). H. M. D.

Magnetic Susceptibility of Alloys of Bismuth and Tin. S. C. LAWS (*Phil. Mag.*, 1904, [vi], 8, 49—57).—The addition of tin to bismuth is accompanied by a diminution of the diamagnetic properties of the metal. As in the case of other properties, the effect is most marked when the proportion of added tin is small.

J. C. P.

New Thermometer for Cryoscopic and Ebullioscopic Measurements at Low Temperatures. GIUSEPPE MAGRI (*Gazzetta*, 1904, 34, i, 387—388).—In carrying out cryoscopic or ebullioscopic measurements in liquefied gases by means of a differential thermometer of the Walferdin type containing methyl alcohol and a drop of mercury as indicator, it sometimes happens that the mercury falls into a position where the temperature is so low as to solidify it. In order to prevent this, and hence any possibility of the bulb being broken when the alcohol becomes warmer and expands, the author introduces into the horizontal tube, near the bend, a small bulb. This is found to act as a perfect safeguard.

T. H. P.

Thermal Properties of Salicylaldehyde. WLADIMIR F. LUGININ (*J. Chim. phys.*, 1904, 2, 1—6).—The specific heat of salicylaldehyde was found to be 0.4540 and the latent heat of vaporisation 74.89 cal. The latter number gives 19.45 for the Trouton constant, a value which, although low, is near to the value 20.3 obtained for benzaldehyde. The compound does not therefore appear to be polymerised, so that the introduction of the hydroxyl group does not here cause polymerisation. The author now considers that it appears probable that polymerisation depends more on the type of compound than on the introduction of a hydroxyl group (*Abstr.*, 1903, ii, 7).

L. M. J.

Congruent and Incongruent Liquid Products in the Case of Double Salts. WILHELM MEYERHOFFER (*Zeit. physikal. Chem.*, 1904, 48, 109—112. Compare *Abstr.*, 1901, ii, 639).—A binary double salt and its components have either one incongruent and one congruent melting point or three congruent melting points. A similar remark applies to salt hydrates, for they have either one incongruent melting point (transition point) and one congruent melting point (cryohydric point) or three congruent melting points, as in the case of the hydrate, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$.

J. C. P.

Boiling Point Apparatus. JOHAN F. EYKMAN (*J. Chim. phys.*, 1904, 2, 47—51).—The paper contains a figure and description of a form of apparatus for the determination of boiling points, in which the solution is heated by the vapour of the pure solvent. The apparatus has the advantage of being entirely of glass, without corks or india-rubber, and its trustworthiness is indicated by tables of results obtained with solutions in various solvents.

L. M. J.

Boiling Points under Different Pressures of Naphthalene, Diphenyl, and Benzophenone. ADRIEN JAQUEROD and EUGÈNE WASSMER (*J. Chim. phys.*, 1904, 2, 52—78).—The boiling points of the three compounds were determined by means of a hydrogen thermometer, and a diagram and description of the apparatus are given. The boiling points were obtained at pressures varying from 300 to 800 mm., and cover a field of temperature ranging from 190° to 308°. Great precautions were taken to ensure accuracy, and examples illustrative of the accuracy of the results are given with the complete tables. The author considers that these compounds should be of great value when a constant temperature between the above limits is required, as they can be more readily purified than those substances the vapour pressure curves of which were determined by Ramsay and Young, and they also suffer no change during the boiling. L. M. J.

The Slope of the Vaporisation Neutral Curve. JOSEPH E. TREVOR (*J. Physical Chem.*, 1904, 8, 341—350).—A mathematical paper in which the form is deduced for the expansion curve in which a diabatic expansion causes neither evaporation nor condensation.

L. M. J.

Vapour Pressures in the System: Benzene, Carbon Tetrachloride, and Ethyl Alcohol. II. FRANS A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 1904, 48, 257—288).—The data recorded in the earlier paper are further discussed and applied. J. C. P.

Cryoscopic Study of Solutions in Sulphide of Antimony. JOSEPH GUINCHANT and PAUL CHRÉTIEN (*Compt. rend.*, 1904, 138, 1269—1272).—The lowering of the temperature of solidification of fused antimony sulphide (540°) on the addition of silver sulphide or lead sulphide has been measured. The two series of data give 790 as the molecular lowering of the freezing point. From the equation $k = 0.02T^2/L$, the heat of fusion of the sulphide is calculated to be 16.7 Cal., which is in good agreement with the value 17.5 Cal. obtained directly by calorimetric measurements.

Metallic antimony dissolves in the molten sulphide, and the lowering of the freezing point produced decreases rapidly with increasing concentration. If, however, the experimental data are extrapolated to zero concentration, the value 113 is obtained as the mol. weight of the dissolved antimony (at. wt. = 120). It is, however, possible that reaction takes place according to the equation $\text{Sb} + \text{Sb}_2\text{S}_3 = \text{Sb}_3\text{S}_3$, and the nature of the solution cannot be definitely determined from the experimental data.

H. M. D.

Thermochemical Considerations. ANTONIO QUARTAROLI (*Gazzetta*, 1904, 34, i, 293—323).—The author attempts to apply the principles of vectors to thermochemical calculation, especially with reference to heats of combination. In this way, he arrives at the following laws: (1) if two elements, *A* and *B*, are capable of yielding two compounds, *AB* and *AB*₂, the coefficient by which it is necessary to multiply the heat of formation of *AB* to obtain the heat developed in the reaction *AB* + *B* will be the smaller as the heat of formation of *AB* becomes

greater. (2) If two elements form different compounds of the types AB , AB_2 , AB_n , the heat developed in the successive combinations tends to become constant, and can only vary appreciably in the case of the first compound. (3) If, however, A is not an element, but a moderately complex radicle, and B an element or radicle much less complex than A , a slight decrease occurs in the heat developed in the reactions $A + B$, $AB + B$, &c.

T. H. P.

Heat of Combustion of Some Polymeric and Isomeric Compounds produced by the Action of Light. C. N. RIIBER and J. SCHETELIG (*Zeit. physikal. Chem.*, 1904, 48, 345—352).—The heats of combustion of the yellow and white cinnamylidenemalonic acids (compare Liebermann, *Abstr.*, 1895, i, 470; Riiber, *Abstr.*, 1902, i, 617) are respectively 6.056 and 6.055 Cal. per gram; those of cinnamic and α -truxillic acids (compare Riiber, *Abstr.*, 1902, i, 785) are 7.047 and 7.039 Cal. per gram. Thus, allowing for the experimental error, there is no energy change involved in the transformations of the above acids. For the sake of comparison, the authors record also the following heats of combustion (per gram substance): tetramethylenedicarboxylic acid, 4.462 Cal. (Stohmann); acrylic acid (solid), 4.534 Cal.; cinnamylideneacetic acid, 7.535 Cal.; *allocinnamylideneacetic acid*, 7.586 Cal. (compare Liebermann, *loc. cit.*).

J. C. P.

Standard of Relative Viscosity. "Negative Viscosity." WILLIAM W. TAYLOR (*Proc. Roy. Soc. Edin.*, 1904, 25, 227—230).—In the formula $\eta = \eta_0 st / s_0 t_0$, where η_0 , s_0 , t_0 are the viscosity, density, and time of flow respectively through a tube of a given volume of a standard liquid, and η , s , t are the corresponding data for the liquid under examination, the viscosity of the solvent at the temperature of the experiment is generally taken as $\eta_0 = 1$. It is suggested that it would be better to take the viscosity of water at 0° as the standard, and to refer the relative viscosity of liquids and solutions to this alone. The bearing of this on "negative viscosity" is indicated.

A. McK.

Viscosity of Aqueous Solutions of Chlorides, Bromides, and Iodides. WILLIAM W. TAYLOR and CLERK RANKEN (*Proc. Roy. Soc. Edin.*, 1904, 25, 231—241).—Taylor and Inglis (*Phil. Mag.*, 1903, [vi], 5, 312) have shown that the rate of evolution of hydrogen from the action of aluminium on sulphuric acid is increased by the addition of a small quantity of potassium chloride, whilst the addition of an equivalent amount of potassium bromide has no effect. Subsequent investigation has shown that, under similar conditions and with solutions of pure hydrochloric acid and hydrobromic acid with the same concentration of hydrogen ions, the rate of evolution of hydrogen from hydrochloric acid is about thirty times as great as from hydrobromic acid. The authors have determined the relative viscosity of solutions of chloride, bromide, and iodide under varying conditions of temperature and concentration with the view of finding whether those marked differences between chloride and bromide mentioned manifest themselves in other physical properties.

The relative viscosity of aqueous solutions of potassium chloride, potassium bromide, potassium iodide, hydrochloric acid, and hydrobromic acid respectively was determined at 0°, 15°, and 25°, and at concentrations of 1 mol., 2 mols., and 3 mols. per litre. The equivalent conductivity of the same solutions at 0° was also determined.

The change of viscosity with change of temperature diminishes from chlorine to bromine and from bromine to iodine. The effect of concentration on the viscosity depends on the temperature; it may affect the viscosity in opposite directions at different temperatures.

There are considerable differences in viscosity of chloride, bromide, and iodide, and especially in the effect of changes in concentration and temperature. A. McK.

Molecular Weights of Liquids. CLARENCE L. SPEYERS (*Amer. J. Sci.*, 1904, [iv], 17, 427—436).—The author considers it undesirable to speak of associated molecules when there is not purely chemical evidence that such association exists. He suggests the term "activity factor" in place of what is generally termed "association factor." When $a > 1$, therefore, depressed chemical activity is to be expected, whilst increased chemical activity termed electrolytic dissociation is indicated by $a < 1$. In a system of two liquid components forming two phases, by application of the formula $n/N = (p - p')/p'$ (see Abstr., 1902, ii, 388), and recollecting that the vapour pressure of each component must be the same in the two phases, the author shows that the activity factor of each liquid is increased by the effect of the other. The activity factors of aniline in mixtures of aniline and amylene are calculated, and it is seen that the factor increases very greatly to a concentration of about 75 per cent. of aniline, after which it decreases. The activity factors of nitrobenzene in various solutions were also calculated; for this compound, the values do not show so great an increase, except in the case of solutions in pentane, in which two phases exist. L. M. J.

Theory of Capillarity. GERRIT BAKKER (*Zeit. physikal. Chem.*, 1904, 48, 1—39).—A physical and mathematical paper. J. C. P.

Velocity of Diffusion of Water through a Semi-permeable Membrane. JOH. ŠEBOR (*Zeit. Elektrochem.*, 1904, 10, 347—353).—A membrane of copper ferrocyanide formed on the outside of a porous cell is used; after very thorough washing with water, the cell is filled with distilled water and immersed in solutions of various substances, and the rate at which water diffuses out of the cell determined by observing the fall of level in a graduated tube attached to the cell. Using solutions of sucrose, it is shown that the rate of diffusion (c.c. per hour) is proportional to the osmotic pressure of the solution. The constant (rate of diffusion/osmotic pressure) is, for a given membrane, the same for all substances (sucrose, dextrose, and mannitol were tried). The constant increases rapidly with the temperature. It is obvious that when the diffusion constant has been found for a given membrane, a measurement of the rate of diffusion through the membrane can be used to calculate the osmotic pressure of the solution, and so to calculate the molecular weight of the dissolved substance.

Several experiments of this kind are made with barium chloride, raffinose, dextrin, and dextrose; the results agree approximately with theory. In the case of dextrose, the osmotic pressure remained unchanged when the rotatory power diminished to about one-half its initial value. T. E.

Anodic Behaviour of Tin, Antimony, and Bismuth. KARL ELBS and H. THÜMMEL (*Zeit. Elektrochem.*, 1904, 10, 364—367).—A tin anode dissolves in solutions of sodium chloride, or sulphate, or hydrochloric or sulphuric acids almost entirely in the stannous condition. Antimony and bismuth, in sodium chloride or hydrochloric acid, dissolve entirely in the trivalent form. T. E.

Saturation by the Method of Air-bubbling. HECTOR R. CARVETH and ROY E. FOWLER (*J. Physical Chem.*, 1904, 8, 313—324).—Experiments were made to determine the accuracy of the method for the determination of the vapour pressure of a solution which consists in the estimation of the moisture carried over when a known volume of air is bubbled through the solution. The authors, from analogy with the solution of salts, considered it probable that the air would be saturated with moisture if it were first nearly saturated at a higher temperature and then passed through the solution at the temperature desired. The experiments were hence carried out thus: dry air was passed through (1) the liquid to be investigated at the desired temperature, (2) the liquid at a higher temperature, (3) liquid as in No. 1, (4) absorption bulbs. The liquid employed was pure water. The results indicate the great difficulty of obtaining accuracy, and that the method requires very careful examination before new results obtained by its use are accepted. L. M. J.

Velocity of Absorption of Gaseous by Solid Substances. ARTHUR HANTZSCH (*Zeit. physikal. Chem.*, 1904, 48, 289—329).—The cases studied were the absorption of ammonia by solid organic acids and of hydrogen chloride by solid organic bases. The absorbent solid was obtained in a finely divided condition by grinding it with powdered glass, and the gas to be absorbed was in some experiments undiluted, in others diluted with air. When the gas is undiluted or present in the diluted form in very large excess, the course of the absorption is in general governed by the equation for a reaction of the first order. When the gas is present in molecular quantity and mixed with air, the course of absorption is governed by the equation for a reaction of the second order.

With acids whose dissociation constants can be readily determined, the absorption velocity constant for ammonia varies with the strength of the absorbent acid, but much less markedly than the dissociation constant; thus, the absorption constant for trichloroacetic acid is only about one and a half times as great as that for monochloroacetic acid under the same conditions, whilst the corresponding dissociation constants are approximately as 1000:1. The value of the absorption constant diminishes rapidly as the initial ammonia concentration diminishes. Absorption constants are obtained also for substances of a very weak acidic character, such as α - and β -naphthols, phenol,

p-cresol, and *antibenzaldoxime*. In these cases, the order of value of the constants is much more distinctly the order of the acidic strength. The fact that an absorption velocity constant can be got at all appears to be characteristic of true acids, for with pseudo-acids no constant can be obtained, as will be shown in detail in a later paper.

Absorption constants for hydrogen chloride with basic substances such as *p*-toluidine, tribromoaniline, α - and β -naphthylamines, carbamide, and benzidine can also be obtained, and their determination furnishes a method of distinguishing true and pseudo-bases. To the absolute values of these absorption velocity constants no great importance is attached, because of their dependence on the conditions of the experiment. J. C. P.

Solubility of Hydrogen and Nitrous Oxide in Water as Affected by Different Dissociated Substances. W. KNORP (*Zeit. physikal. Chem.*, 1904, 48, 97—108. Compare Braun, Abstr., 1900, ii, 529).—The author finds the coefficient of absorption of hydrogen in pure water at 20° to be 0.01883, of nitrous oxide 0.6270. The solubility of hydrogen in solutions of chloral hydrate diminishes almost in a linear manner with the concentration of the latter. In solutions also of ammonium, sodium, and potassium nitrates and potassium chloride, the absorption coefficient is lowered, the extent of the lowering being greater for sodium nitrate than for potassium nitrate, greater for potassium nitrate than for ammonium nitrate, and greater for potassium chloride than for potassium nitrate. From the equation $1/c \cdot \log C_1'/C_1 = (1 - \gamma)A - \gamma B$, where A and B are constants, c and γ the molecular concentration and degree of dissociation of the electrolyte, C_1' and C_1 the molecular concentrations of the gas in salt solution and water respectively, it is possible to calculate the absorption coefficient in good agreement with experiment. On the other hand, the values of the expression $(a - a')/M^{2/3}$ are not satisfactorily constant, no better than those of the expression $(a - a')/M$.

In chloral hydrate solutions, the absorption coefficient of nitrous oxide diminishes in a linear manner with the concentration of the chloral hydrate. In propionic acid solutions, however, it actually increases with the concentration of the acid, and for the medium concentrations the values of $1/n_2 \cdot \log C_1'/C_1$ are constant (n_2 = number of molecules of acid). For nitrous oxide in solutions of sodium and potassium nitrates, the equation $1/c \cdot \log C_1'/C_1 = (1 - \gamma)A - \gamma B$ is found to be applicable. J. C. P.

Theory of the Saturation Phenomena of Binary Mixtures. P. BOEDKE (*Zeit. physikal. Chem.*, 1904, 48, 330—344).—A theoretical paper, in which the author, starting from the critical solution phenomena, arrives at an extension of the solution laws. In particular, it is shown that on the basis of the dilute solution laws and the law of the rectilinear diameter, it is possible to formulate the saturation relationships of certain binary liquid mixtures in good agreement with experiment (compare Rothmund, Abstr., 1898, ii, 503). J. C. P.

Lowering of Solubility. I. HANS EULER (*Arkiv. Kem. Min. Geol.*, 1904, 1, 143—158).—Attention is drawn to the parallel effects

of different electrolytes, such as lithium chloride, potassium nitrate and chloride, in lowering the solubilities of hydrogen, nitrous oxide, and ethyl acetate in water. A consideration of the experimental data leads to the conclusion that the equivalent lowering of the solubility is an additive property of the two dissolved substances. It is shown that when l_0 and l are the solubilities in water and in the salt solution respectively, and c is the concentration of the salt, then $(l_0 - l)/c^{3/4} = \text{const.}$

The author has studied also the extent to which the solubilities of two salts with a common ion are mutually affected. The pairs of salts chosen are such as crystallise without water of crystallisation.

J. C. P.

Rate of Dissolution of Salts in their Aqueous Solutions. J. SCHÜRR (*J. Chim. phys.*, 1904, 2, 245—306).—The rate of dissolution was measured by determination of the successive times in which the crystal suspended in the liquid lost 0.01 gram in weight (apparent weight). The crystals in each case were covered with paraffin except one plane face, and the rate of dissolution was calculated as dN/dt , where N is the thickness of the crystal normally to this face. Three periods are distinguished during the dissolution: (1) preliminary period, (2) period of steady state, (3) period in which the action is irregular owing to the exaggerated deformations of the crystal face. During the first period there are formed on the face of the crystal corrosion figures; these depend on the nature of the crystal and its crystallographic face; some of these increase in size, whilst others may decrease, and after a short time they give place to what the author terms convection striæ, which appear during the second period; these striæ characterise the convection currents during the steady state; they are dependent on the position of the face in the solvent, but do not differ for the different crystallographic faces. During this period, the striæ, as also the rate of dissolution, differ but little in different crystals of the same compound. Gentle agitation of the liquid was found to have little or no effect on the dissolution. The variation of the rate of dissolution with concentration was investigated, and the results are in accord with the law that the rate of dissolution is proportional to the difference between the logarithm of the saturation concentration and of the actual concentration. This law the author further supports by theoretical considerations, but it is obviously inapplicable for the limiting case of infinite dilution. In the particular case of a very slightly soluble salt, the logarithms may be replaced by the actual concentrations; the expression $dx/dt = A \log x_0/x$ becoming $dx/dt = A(x_0 - x)$, the form of expression deduced by Noyes and Whitney. Further experiments, however, proved that this expression is not valid for more soluble salts. Experiments were then made on the rate of dissolution in solutions of other salts with one common ion. Very marked differences are found for dissolution of copper sulphate in solutions of potassium and ammonium sulphates, and the author considers that the effect of the metal is more pronounced than that of the acid radicle. In a few cases, the temperature-coefficient between 10° and 30° was obtained, and an expression of the form

$(dN/dt) = (dN/dt)(1 + at + bt^2)$ is given, where a varies from 0.03 to 0.04, and b from 0.015 to 0.02. L. M. J.

Determination of the Solubility of Salts of Weak Acids from Measurement of their Conductivity. D. GARDNER and D. G. GERASSIMOFF (*Zeit. physikal. Chem.*, 1904, 48, 359—364).—Kohlrausch has recently (Abstr., 1903, ii, 528) published a large number of values for the conductivity of sparingly soluble salts, these values to form a basis for the calculation of their solubility. The authors point out that if the salt is derived from a weak acid, hydrolysis, resulting in an excess of OH^- ions, will take place, and thus the conductivity will not be a measure of the solubility. In the special case of barium carbonate, they show that the conductivity of the saturated solution diminishes in presence of increasing quantities of sodium hydroxide, until it reaches a limiting value about 6×10^{-6} , instead of the value 28.6×10^{-6} obtained in pure water. It is shown, on the other hand, that the conductivity of barium sulphate, the hydrolysis of which is negligible, is scarcely affected by the presence of sodium hydroxide.

J. C. P.

Solutions of Salts of Ammonia and of Amines. HANS EULER (*Arkiv. Kem. Min. Geol.*, 1904, 1, 133—142).—The author's measurements of the solubility of aniline in water show that 100 grams of water at 18° dissolve 3.61 grams of aniline. The solubility of aniline in solutions of certain chlorides and of sodium and potassium hydroxides of various strengths was also determined. The diminutions in the solubility rest for the most part on the physical action which in general determines "salting-out" (see Abstr., 1900, ii, 196). In the case of ammonia, however, the formation of complex compounds plays a greater part. The freezing point depressions of solutions of aniline and its hydrochloride in water have been determined; when the base and the salt are both present in low concentrations, the formation of complex compounds is slight, but this becomes more marked in the more concentrated solutions.

The results show that whilst aniline forms, with metallic salts, much less stable complexes than ammonia, yet the proportion of complex salt formed is much greater with aniline than with ammonia. Analogy is drawn between compounds such as $\text{NH}_4\text{NO}_3, \text{NH}_3$ and $\text{AgNO}_3, 2\text{NH}_3$.

T. H. P.

Solubility of Calcium Sulphate in Aqueous Solutions of Potassium and Sodium Sulphates. FRANK K. CAMERON and J. F. BREAZEALE (*J. Physical Chem.*, 1904, 8, 335—340).—The curve for the solubility of calcium sulphate in solutions of potassium sulphate, drawn with concentrations of calcium sulphate as ordinates and of potassium sulphate as abscissæ is seen to consist of two portions, one in which gypsum is the solid phase, the other in which syngenite is the solid phase. The triple point was found to correspond with the concentrations: potassium sulphate, 32.47 grams; calcium sulphate, 1.582 grams per litre. The first curve has a minimum at about the concentration potassium sulphate, 12 grams, calcium sulphate, 1.45 grams

per litre (approximately); the second curve has no minimum, the concentration of the calcium sulphate decreasing from the triple point as that of the potassium sulphate increases. In solutions of sodium sulphate, a continuous curve is obtained with a minimum at about 15 per cent. of sodium sulphate. The temperature in both cases was 25°.

L. M. J.

Solid Solutions between Nitro- and Nitroso-derivatives. GIUSEPPE BRUNI and A. CALLEGARI (*Atti R. Accad. Lincei*, 1904, [v], 13, i, 567—573).—The authors have made cryoscopic measurements of: (1) nitrosobenzene in benzene and nitrobenzene; (2) *p*-nitrosotoluene in nitrobenzene and *p*-nitrotoluene; (3) ethyl *o*-nitrosobenzoate in ethyl *o*-nitrobenzoate, and (4) *o*-nitrobenzaldehyde in *o*-nitrosobenzoic acid. From the results obtained, they draw the following conclusions: (1) aromatic nitroso-derivatives in general give solid solutions with the corresponding nitro-derivatives. (2) Since the depressions are always proportional to the concentrations, and the coefficient of distribution between the two phases hence constant, the nitroso-derivatives have the simple molecular weight in such solid solutions. (3) The solid solutions, like the liquid ones, of the true nitroso-derivatives, are coloured green. (4) An acid can form solid solutions with the corresponding aldehyde. (5) It is possible to obtain solid solutions (super-saturated) in the case when the solute is not soluble in the liquid solvent.

p-Nitrosodiethylaniline forms mixed crystals with *p*-nitrodiethylaniline, and hence, in the crystalline state, has the structure of a true nitroso-derivative, although in the dissolved or molten condition it has the tautomeric quinonoid configuration. The slowness of crystallisation and the irregular cryoscopic results obtained indicate the existence, in this case, of two kinds of tautomeric molecules in the liquid phase.

The relations met with between organic nitro- and nitroso-compounds probably exist also between inorganic nitrites and nitrates (compare Müller, this vol., ii, 117).

T. H. P.

Freezing of Solutions in Dimorphous Solvents. GIUSEPPE BRUNI and A. CALLEGARI (*Atti R. Accad. Lincei*, 1904, [v], 13, i, 481—489).—Assuming that a dissolved substance does not form solid solutions with either of the two modifications of a dimorphous solvent, the authors discuss, with reference to vapour pressure-temperature diagrams, the cases of the solvent being (1) enantiotropically dimorphous and (2) monotropically dimorphous. The freezing point depression is, for case (1), greater for the stable than for the labile form; when the solution is very concentrated, the separation of the labile form may correspond with a higher freezing point than that of the stable modification. In case (2), however, the depression for the labile form is greater than for the stable one. In this way, information can be obtained regarding the character of the dimorphism of a solvent.

Knowing the freezing points of the two forms, the three transition points (T_1 , T_2 , and T_3), and also the cryoscopic constant (and hence the

heat of fusion, Q_1), for one modification, the heat of transformation can be calculated from van't Hoff's equation: $Q_2/T_2 = Q_1/T_1 + Q_3/T_3$.

For the stable form of methylene iodide, the authors obtain the freezing point 5.7° , which agrees well with the value 5.71° obtained by Tammann and Hollmann (Tammann, *Kristallisieren und Schmelzen*, 1903, pp. 278 *et seq.*), but is considerably higher than that given by Beckmann (this vol., ii, 235), namely, 4.7° ; the labile modification has the freezing point 5.23° . The heats of fusion of the two forms are 10.8° and 11.3° respectively, so that the heat of transformation is 0.5 . These numbers are in accord with van't Hoff's equation.

The stable form of *o*-nitrobenzaldehyde has the freezing point 43.0° , and the molecular freezing point depression 72 , the corresponding numbers for the labile modification being 40.4° and 79 respectively; this aldehyde is hence monotropically dimorphous. The same is the case for iodine monochloride.

T. H. P.

Determination by an Iodometric Method of the Degree of Hydrolytic Decomposition of Salts. WLADIMIR E. PAWLOFF and D. G. GERASSIMOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 566—572).—A preliminary paper, describing a method by which the degree of hydrolytic dissociation of salts is measured by determining the amount of iodine evolved when the salt is mixed with potassium iodide and iodate. The results obtained with a number of salts and with sulphuric acid are given in tabular form.

T. H. P.

Phenomena of Flocculent Precipitation. M. NEISSER and U. FRIEDEMANN (*Chem. Centr.*, 1904, i, 1387—1388; from *Münch. med. Woch.*, 51, No. 11).—The particles of mastic in an aqueous emulsion formed by pouring an alcoholic solution into water are electro-negatively charged, for when subjected to a high *E.M.F.* between platinum electrodes they move to the anode and are precipitated there. The addition of small quantities of acids or salts to such an emulsion causes the particles to be precipitated in a flocculent form. Experiments have been made on the action of aluminium sulphate, ferric chloride, ferric nitrate, colloidal ferric hydroxide, arsenic trisulphide, and ferric hydroxide. The results show that when colloids and suspensions which are charged with different kinds of electricity are brought together in certain proportions, both separate in a flocculent form. Aniline dyes behave in this respect like colloids. The acid dyes which were examined were found to move towards the anode and the basic towards the cathode; the latter cause the precipitation of mastic. When arsenic trisulphide benzopurpurin, eosin, Bismarck-brown, neutral-red, methylene-blue, or positively charged colloidal ferric hydroxide is added to an excess of the negatively charged mastic, precipitation is prevented and no separation of the small quantity of colloid in a flocculent form could be detected. This inhibiting effect may be due to the coating of the one colloid or suspension by the other, whereby the former is protected from the action of the salt ions. In the zone affected, the inhibiting colloid only appears to be present, the second being in a form which cannot be detected by reactions depending on precipitation. Gelatin,

serum, extract of leeches or bacteria and albuminous colloids also prevent the precipitation of negatively charged suspensions and colloids by substances by which they are not themselves precipitated. Although these colloids do not cause flocculent precipitation, they acquire this power when salts are added in quantities which are in themselves insufficient to cause precipitation. The albuminous colloids may be regarded as mixtures or as colloids which, unlike the metallic colloids, may possess both electro-positive and electro-negative properties. By the addition of small quantities of salts, the amphoteric colloids become positively or negatively charged, and then behave like the metallic colloids; a small quantity then causes flocculent precipitation of suspensions which have opposite electric charges, whilst a larger quantity prevents it. In its physical aspect, flocculent precipitation, like agglutination, appears to be a link between the phenomena of precipitation of albuminous substances and that of inorganic suspensions.

E. W. W.

Experiments on the Precipitation with Colloidal Solutions of Metal Sulphides. ARTHUR MÜLLER and PAUL ARTMANN (*Chem. Centr.*, 1904, i, 1388; from *Oesterr. Chem. Zeit.*, 7, 149—151. Compare Zsigmondy, *Abstr.*, 1902, ii, 188).—Experiments made with colloidal solutions of the sulphides of arsenic, cadmium, and silver have shown that in these cases the addition of gum and casein prevents the precipitation of the sulphides by acids or salts much more effectively than either glue or isinglass. This may depend on the fact that under certain conditions the solutions of the sulphides of arsenic and cadmium form precipitates with solutions of glue.

E. W. W.

Formation of Precipitates in Gelatin. JOACHIM HAUSMANN (*Zeit. anorg. Chem.*, 1904, 40, 110—145).—A solution of a particular salt in gelatin was allowed to solidify in a small test-tube, which was then immersed in a vessel containing an aqueous solution of a second salt, which is capable of interacting with the first salt to give a precipitate. In such cases, Liesegang had previously observed that the precipitate gradually forms in the gelatin, not uniformly, but in layers; the author has examined a large number of salts to find out whether this phenomenon is a general one. The experiments were carried out at the temperature of the laboratory. The appearance of the various rings observed is represented by reproductions from photographs. In the case of silver dichromate, formed from silver nitrate and potassium dichromate, the layers were brown, and the intervening spaces became coloured with a substance lighter in colour than that of the rings, from which secondary rings gradually separated. The following precipitates were examined: silver chloride, silver bromide, silver iodide, silver thiocyanate, silver iodate, silver orthophosphate, silver pyrophosphate, lead chloride, lead iodide, lead sulphate, mercurous chloride, mercurous iodide, copper thiocyanate, copper hydroxide, lead sulphide, mercuric sulphide, silver sulphide, copper sulphide, &c. All the sulphides examined were obtained in the colloidal form in the gelatin when sodium sulphide was used as the precipitant; when,

however, ammonium sulphide was used, the precipitates were more or less compact and of definite structure.

In almost all the cases examined, layers of the precipitate were formed in the gelatin; exceptions were the sulphates of barium, strontium, and calcium, the oxalates of barium and silver, and the chloride, bromide, and iodide of thallium, which formed crystals distributed throughout the gelatin.

The formation of the various precipitates in layer took place more readily in gelatin than in agar-agar or starch.

The rate at which the layers formed with various salts was studied. For equivalent dilute solutions of various chlorides, the precipitate in the gelatin (containing silver nitrate) rises to the same height in each case, whilst the rate of the action depends on the chlorion and not on the cathion with the particular chloride used. The height to which the precipitate rises is, on the other hand, dependent on the cathion of the salt dissolved in the gelatin, that is, on the silver ion, and is independent of the anion.

This method is the first one which is not electrolytic for determining the speed of ions.

A. McK.

Formation and Transition of Liquid Mixed Crystals. ARNOLD C. DE KOCK (*Zeit. physikal. Chem.*, 1904, 48, 129—176).—Solid *p*-azoxyanisole assumes the crystalline liquid condition (turbid) at 114°, and becomes a clear liquid at 135·2°. A similar substance is *p*-methoxycinnamic acid, for which the corresponding temperatures are 170·6° and 185·5°. When these two substances are mixed, the melting points (135·2° and 185·5°) are lowered; the temperature-concentration curve exhibits a rounded minimum, and shows that homogeneous liquid mixed crystals are formed in a continuous series. At certain lower temperatures, varying with the composition of the mixture, one or other of the pure solid substances is deposited, and the temperature-concentration curve based on these observations resembles an ordinary freezing point curve with a eutectic point at 107—108°. Similar experiments have been made with binary systems, only one component of which forms a crystalline liquid, namely, (1) *p*-azoxyanisole and quinol, (2) *p*-methoxycinnamic acid and quinol, (3) *p*-azoxyanisole and benzophenone, (4) ethyl *p*-azoxybenzoate and ethyl *p*-azobenzoate. In these cases also liquid mixed crystals are formed, but only up to a certain concentration of the second substance. The temperature at which *p*-azoxyanisole passes from the turbid crystalline liquid condition to the ordinary clear non-crystalline liquid condition is lowered by the addition of quinol or benzophenone. The value of the molecular depression is approximately the same (about 4900) in the two cases, provided allowance is made for the amount of quinol or benzophenone present in the mixed crystals. Using Rothmund's formula (*Abstr.*, 1898, ii, 158), the author has calculated the latent heat of the change crystalline liquid → non-crystalline liquid for *p*-azoxyanisole, and finds the value 0·68 Cal., in good agreement with Hulett.

The manner in which in the above-mentioned liquid mixed crystals are formed, and at lower temperatures pass into ordinary crystals, gives

considerable support to the view that a crystalline liquid is a homogeneous phase, and not an emulsion of two liquids. The author has repeated Tamman's sedimentation experiments (Abstr., 1902, ii, 445) with another sample of *p*-azoxyanisole, but cannot confirm that worker's observations. J. C. P.

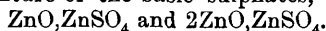
Free Energy of Formation of some Reactions of Technical Importance. HANS VON JÜPTNER (*Zeit. anorg. Chem.*, 1904, 40, 61—64. Compare this vol., ii, 382).—The free energy of formation of carbon dioxide from amorphous carbon and oxygen is calculated from Le Chatelier's determinations. A. McK.

Significance of the Coefficient *B* in the Expression for the Alteration of Free Energy. HANS VON JÜPTNER (*Zeit. anorg. Chem.*, 1904, 40, 65—67).—The alteration of the free energy in any reaction is represented by $A_T = A_0 + BT - 2.30259(a_2 - a_1)T \log T - (\beta_2 - \beta_1)T^2 - (\gamma_2 - \gamma_1)/T^3$ (compare this vol., ii, 382). In this expression, $B = R \times \text{constant}$, that is, the product of the gas constant R ($= 1.982$ cal.) and another constant, deduced by integration from the van't Hoff equation,

$$dlk = -Q_T dT/RT^2, \text{ namely,} \\ \int Q_T dT/RT^2 + lk = \text{constant.}$$

Instances are quoted where this constant is calculated. A. McK.

Metallic Substitution. ALB. J. J. VANDEVELDE and C. E. WASTEELS (*Bull. Acad. Roy. Belg.*, 1904, 331—360. Compare Abstr., 1903, ii, 200).—The authors have extended their investigation of the various factors which influence the velocity of reaction between metallic zinc and aqueous and dilute alcoholic solutions of copper sulphate to the effect of temperature and of the concentration of the alcohol. They find that the initial velocity of reaction, as measured by the loss of weight of the fragment of metallic zinc added, increases with rise of temperature and diminishes with increasing concentration of the alcohol. After a sufficient lapse of time, however, the velocity of reaction, measured in the same way, is greatest in the solution containing most alcohol, and the period necessary to produce this change is least at the lowest temperature employed. This abnormal behaviour is shown to be due to the fact that in the earlier stages of the reaction simple substitution of copper by zinc occurs, but that after the whole of the copper has been deposited the zinc in solution begins to be precipitated as a mixture of the basic sulphates,



No precipitation of basic sulphate occurs when metallic zinc is placed in a solution of zinc sulphate.

Magnesium, on the other hand, when placed in aqueous solutions of its sulphate, furnishes basic precipitates (Lemoine, Abstr., 1899, ii, 656, and Tommasi, *ibid.*, 1900, ii, 16). The authors have repeated Kahlenberg's experiments (Abstr., 1903, ii, 426), and find that when the velocity of reaction of magnesium with water and dilute alcohol

is measured by the quantity of hydrogen evolved, varying results are obtained from which no conclusion can be drawn (compare Roberts and Brown, *Abstr.*, 1903, ii, 726). T. A. H.

Theory of Pseudo-acids. HUGO KAUFMANN (*Ber.*, 1904, 37, 2468—2469. Compare this vol., ii, 326).—The author's conclusion that the salts of pseudo-acids are normally hydrolysed to the same extent as those of ordinary acids having the same dissociation constant is shown to be consistent with the results obtained by von Zawidzki (this vol., ii, 475). The objections raised by the latter author are due to a confusion between the constant K obtained by him with the true constant of hydrolytic dissociation K' . C. H. D.

Stability of Equilibrium of a Homogeneous Phase. PAUL SAUREL (*J. Physical Chem.*, 1904, 8, 325—334).—A mathematical paper in which results previously obtained by Gibbs are obtained by other methods. The author starts from the equation representing the energy, e , of a homogeneous phase in equilibrium as a one valued function of its entropy, η , its volume, v , and the masses, m_1, m_2 , &c., of its independent components, that is, $\epsilon = f(\eta, v, m_1, m_2, \dots, m_n)$. Many equations are developed, two expressing the statements:

(1) If a homogeneous phase of constant mass in stable equilibrium is heated or cooled under constant pressure or volume, the changes in temperature and in entropy have the same sign, and (2) if such a phase is compressed or expanded isothermally or adiabatically, the changes in pressure and volume have opposite signs. L. M. J.

Equilibrium Curves in the System: *p*-Bromotoluene—*p*-Dibromobenzene. W. BORODOWSKY and A. D. BOGOJAWLENSKY (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 559—566).—Previous work of Bogojawlensky on the specific heats of mixtures of *p*-bromotoluene and *p*-dibromobenzene having indicated a peculiarity in the melting point curves for these substances, the authors have investigated these curves. The diagram of condition for mixtures of these two compounds is formed by the superposition of two types of melting point curve: (1) a curve for isomorphous substances—mixtures of *p*-bromotoluene with *p*-dibromobenzene, and (2) a curve for substances forming a eutectic mixture—mixtures of *p*-dibromobenzene with *p*-bromotoluene. From the course taken by the melting point curve, it is evident that the mixtures represent an example of incomplete isodimorphism or one-sided miscibility of two kinds of crystals. One part of the diagram corresponds with the eutectic mixture; at 36.8°, a crystalline mixture of the composition $2C_7H_7Br, C_6H_4Br_2$ is deposited, whilst the remainder of the diagram corresponds with the formation of isomorphous mixed crystals.

The authors have also studied the boiling point curve and the curve of vapour composition for different mixtures of *p*-dibromobenzene and *p*-bromotoluene. These curves confirm the existence of this new form of equilibrium for binary crystalline mixtures. T. H. P.

Action of Bromine on Acetaldehyde in Aqueous Solution. STEFAN BUGARSZKY (*Zeit. physikal. Chem.*, 1904, 48, 63—86).—The author shows that in dilute aqueous solution the interaction of bromine and acetaldehyde is represented by the equation $C_2H_4O + Br_2 + H_2O = 2HBr + C_2H_4O_2$. The change takes place with measurable velocity, and its course may be followed by determining the unchanged bromine at intervals. That the bromine does not replace any hydrogen atoms in the aldehyde molecule is shown by the observation that the acidity of the reaction mixture (in gram-equivalents per litre) is always 1.5 times the bromine concentration (in the same unit). So long as the solution is dilute, the reaction conforms to the bimolecular type. At higher values of the bromine concentration, the simple course of the reaction is disturbed owing to the fact that the hydrogen bromide formed in the reaction fixes a certain portion of the bromine. When allowance is made for this in a manner previously adopted (Abstr., 1902, ii, 9), the bimolecular character of the reaction is again evident. When the concentration is expressed in mols. per litre, and the minute is the unit of time, the values of the velocity-coefficient, k , at various temperatures, t , are as follows :

| t° . | k . |
|-------------|-------|
| 0 | 0.117 |
| 10 | 0.308 |
| 20 | 0.790 |
| 25 | 1.205 |

That is, for a rise of 10° , the velocity-coefficient increases in the ratio 2.6:1. Further, the variation of the velocity-coefficient with temperature is satisfactorily represented by the equation :
 $\log k = 0.04068t - 0.9257$.
 J. C. P.

Kinetics of Sugar Inversion. JOSEPH W. MELLOR and L. BRADSHAW (*Zeit. physikal. Chem.*, 1904, 48, 353—358).—A formula is deduced for the course of inversion of sucrose on the hypothesis that the lævulose and dextrose produced by the inversion are birotating. From this point of view, the process of inversion is a primary reaction of the first order on which two secondary reactions, also of the first order, are superposed. The formula obtained is shown to reproduce the experimental data in a satisfactory manner. A somewhat parallel case seems to be the hydrolysis of gentianose, which process, as shown by Bourquelot, takes place in two stages in presence of invertase and emulsin.
 J. C. P.

Enzyme Action. H. P. BARENDRECHT (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 7, 2—18).—When a given quantity of acid acts for a given time on a sugar solution, the amount of inversion is proportional to the initial concentration of the sugar. In the case of enzymes, however, the curve obtained by plotting the amount of inversion in a given time against the initial sugar concentration is not straight throughout, but after a certain value of the initial concentration becomes parallel to the horizontal axis. This peculiarity of enzyme

action has originated the hypothesis on which the author works, namely, that enzymes exert their catalytic action by radiation. So long as the sugar solution is concentrated enough to absorb within a reasonable distance all radiation emanating from an enzyme particle, each particle must exert the same action. In dilute solutions, however, a part of the radiation is absorbed by the water, or when it arrives at a sugar molecule is too weakened to cause inversion. The quantity of sucrose inverted by a given amount of enzyme will, therefore, go on decreasing until a point is reached where, within the sphere of action of an enzyme particle, two sugar molecules can no longer shade each other. From this point, the inversion due to a given quantity of enzyme will be proportional to the sucrose concentration. Experiments show that the inversion of sucrose by invertase is retarded equally by dextrose, lævulose, and invert sugar, that is, these substances absorb the enzyme radiation. When allowance is made for this, it is possible to formulate accurately the course of inversion under the action of invertase.

It is to be expected that the enzyme radiation should have also a synthetical action, and the fact that it cannot ordinarily be detected is probably due in the first place to the secondary change of the decomposition products, at least in the case of invertase. It may be supposed that the reversal phenomena would be observed if the original products of inversion were unchanged, and an equilibrium would then be established. If such a large quantity of enzyme is introduced that this equilibrium point is reached before the birotatory glucose has been converted to any great extent into ordinary glucose, the curve indicating the process of inversion will alter its course at that point, and thereafter the formation of fresh α -glucose will be dominated by the velocity of the conversion of the total α -glucose present into β -glucose. Those equilibria phenomena are observed more readily in the inversion of maltose by yeast extract. J. C. P.

The Reaction induced by an Indirectly Oxidising Ferment (Peroxydase). ÉMILE BOURQUELOT and L. MARCHADIER (*Compt. rend.*, 1904, 138, 1432—1434).—The authors find that the action of a peroxydase in the presence of hydrogen peroxide on vanillin is the same as that of an oxydase in the presence of air; the peroxydase employed was that present in macerated oatmeal, and the product obtained was dehydrodivanillin (compare Lerat, this vol., i, 360), identified by means of its melting point and dimethyl derivative. In this reaction, the hydrogen peroxide cannot be replaced by manganese dioxide. The oxydase and peroxydase further resemble one another in their action in that they are not affected by the presence of a large proportion (50 per cent.) of alcohol, they are paralysed by the presence of a small proportion of hydrocyanic acid, and they resist the action of heat for a longer period of time than the hydrolytic ferments. In explanation of these facts, the authors refer to the hypothesis of the mixed nature of the peroxydases (compare Chodat and Bach, *Abstr.*, 1903, i, 378), and suggest that the peroxydase contains (1) a *hydroxydase* capable, in the presence of air, of converting water into hydrogen peroxide, or giving peroxides with certain substances, and (2) an

indirect oxydase capable of decomposing the peroxides with production of active oxygen. M. A. W.

New Conception of the Chemical Atom. P. DE HEEN (*Bull. Acad. Roy. Belg.*, 1904, 285—289).—The atom is defined as the constant quantity of energy which a given volume of an elementary substance in the gaseous state possesses under the same conditions. If this energy be taken as unity, then the atomic weights are the relative weights of the elements which contain this constant quantity of energy. Physically, an atom may be regarded as composed of rotating fibres of infinite length, in number at least equivalent to the lines in the spectrum of the element, and each having a definite energy of rotation and exercising for equal lengths the same pressure.

Combination between molecular proportions of two monatomic univalent gases would imply that the gyrostats of fibres would join two by two, and the volume of the product would be one-half that of the total volume of the two reacting gases. Since two welded gyrostats would transform the same amount of energy of rotation into energy of translation as a single gyrostat, the same conception may be extended to combination between diatomic and polyatomic gases. Here it may be supposed that the two gyrostats (represented graphically in the original by a disjointed circle of arrows) become iodynamic by some external influence, and the electrons liberated from each gyrostat form an intermediate chain, which exerts a tension and eventually brings the two gyrostats into the tangential position.

It follows from this view that the reactivity of a substance will depend on the facility with which it becomes iodynamic, that if the orientation of its electrons corresponds with that of the cathode rays, the substance will be electro-negative, and if the orientation is converse, electro-positive, and that the maximum valency of a substance will depend on the number of electrons present in each atom. The application of this idea becomes simpler if it is supposed that all gases under the same conditions possess the same length of fibre, that is, have the same number of molecules, and that each atom consists of a single infinitely long, unique, gyrating fibre having distributed about its axis as many twists of different diameters and tensions as there are lines in the spectrum of the element. A molecule in the same way may be regarded as a compound fibre or cable composed of atomic gyrostats, some of which may be left and others right. In the solid form of a compound, the cable is rolled on itself and the nature of its optical activity will depend on the direction in which the cable is coiled.

T. A. H.

International Atomic Weights. JOJI SAKURAI and KIKUNAYE IKEDA (*Chem. News*, 1904, 89, 305).—A letter sent by the authors, as representing the Tokio Chemical Society, to Prof. F. W. Clarke, Chairman of the International Sub-committee, protesting against the introduction of the hydrogen standard in the recent tables of atomic weights, notwithstanding that the larger Committee, from which the sub-Committee was formed, decided to use exclusively the weights based on the oxygen standard.

J. C. P.

Limits of Sensitiveness of Odours and Emanations. MARCELLIN BERTHELOT (*Compt. rend.*, 1904, 138, 1249—1251. Compare Abstr., 1901, ii, 406).—The odour of iodoform is perceptible when 1 gram of the substance loses one-billionth of a gram in an hour. In a hundred years, the loss of weight from 1 gram under the author's conditions of experiment would be less than 1 milligram. In the case of musk, the loss of weight associated with the perception of the odour is possibly a thousand times smaller. On the basis of these data, the author considers it unreasonable to infer that a chemical element has been decomposed because certain very sensitive properties (such as the spectroscopic lines), peculiar to a second element, make their appearance. Minute traces of the second element in the substance examined are more likely to be the cause of the phenomenon. H. M. D.

A Mechanical Model to Illustrate the Gas Laws. FRANK B. KENRICK (*J. Physical Chem.*, 1904, 8, 351—356).—The author, considering that there is great difficulty in getting elementary students to grasp the ideas of the gas laws, Carnot's cycle, the entropy function, &c., has devised a mechanical model, by which these relationships may be illustrated. The model, which is described with the aid of a diagram, has been in use in his laboratory, and an example of a problem worked out with it is given. L. M. J.

Apparatus for Removing Volatile Matters by a Current of Steam. M. EMMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1904, 9, 209—210).—A tubular flask has near the top of its neck a side-tube (which can be attached to a condenser), whilst lower down a tube reaching to the bottom of the flask is attached internally. The liquid from which volatile matter is to be removed is placed in the flask, which is then, by means of a split cork, placed between the two tubes, fixed in the neck of a balloon, the lower part of the flask being immersed in the water, or other liquid in the balloon. On heating the liquid in the balloon to ebullition, the vapour passes down the internal tube, through the contents of the flask, and escapes through the upper side-tube. L. DE K.

Extraction Apparatus and Condensers. HERBERT E. DURHAM (*Proc. physiol. Soc.*, 1904, xxvii—xxxi; *J. Physiol.*, 31).—A simplification of apparatus for extraction. The principle of the condenser used is that the cooling apparatus is placed internally. The apparatus is fully explained with diagrams. W. D. H.

Reflux Condenser with Outer and Inner Cooling Arrangement. ANTON LANDSIEDL (*Chem. Zeit.*, 1904, 28, 598).—A description of a new form of reflux condenser in which the water passes first through a coil of glass tubing placed within the condenser tube and then through the usual outer jacket. A. MCK.

New Laboratory Apparatus. ULRICH (*Chem. Zeit.*, 1904, 28, 598).—The author has devised a new Allihn condenser, wholly made of glass and consisting of an outer jacket, a condensing tube, and a

second refrigerating tube sealed to the condensing tube. The inner tube is connected with the outer one in such a manner that the water may pass from the outer tube through the inner one, so causing a double refrigeration.

A convenient gas-generating apparatus is described, which dispenses with the usual drying or absorbing tubes. The instrument, which takes up little room, consists of a generating vessel with two drying or absorption apparatus vertically placed on it, the whole forming a single apparatus.

L. DE K.

An Improved Portable Gas Generator. HERBERT MCCOY (*Ber.*, 1904, 37, 2534—2536).—A modification of Ostwald's generator, which has the advantage of being portable. For details, the original should be consulted.

W. A. D.

New Form of U-Tube. ROMUALD NOWICKI (*Chem. Zeit.*, 1904, 28, 622).—The U-tube described, it is claimed, has advantages not possessed by the ordinary type.

A. McK.

A New Apparatus for Washing and Absorbing Gases. OTTO SCHEUER (*Chem. Zeit.*, 1904, 28, 598—599).—A single tube is so bent that the gas passes in a fine stream of bubbles through three or more layers of the absorbing liquid. Stoppers are provided, so that the liquid in each section can be independently added or removed by means of a pipette.

A. McK.

Form of Absorption Apparatus. ROMUALD NOWICKI (*Chem. Zeit.*, 1904, 28, 644).—A description of a convenient form of gas absorption apparatus, which consists essentially of two similar upright absorption vessels. The entering tube reaches nearly to the bottom of the vessel, and is at the end drawn out to a fine orifice. This end enters into the lower opening of a coil of glass tubing standing vertically in the absorbing liquid. The stream of gas acts in the coil like an injector, causing a steady current of the absorbing liquid. The exit tube from the first cylinder is connected to the entering tube of the second. The cylinders are filled with the same or different absorbents as needed.

A. McK.

A New Form of Pipette. CARL MEYER (*Zeit. öffentl. Chem.*, 1904, 10, 227).—A graduated pipette has a narrow tube passing down its centre. The lower end of the tube is tapered, so as to close the outlet of the pipette. The top of the tube is closed, and an india-rubber band at the top of the pipette holds the two together. The pipette is widened into a bulb just above the graduated portion, and a side-tube leads from the bulb. The pipette is filled by aspirating with the mouth at the side-tube. The solution passes up the inner tube, and then through a small hole in the latter placed at the zero point of the pipette. When filled, any excess of solution above the zero point runs back through the inner tube. To empty the pipette, either completely or partially, the inner tube is slightly raised.

W. P. S.

Inorganic Chemistry.

Atomic Weight of Iodine. PAUL KÖTHNER and E. AEUER (*Ber.*, 1904, 37, 2536—2538).—Silver iodide, purified by Stas' treatment, gave by Ladenburg's method (*Abstr.*, 1902, ii, 314, 498) an atomic weight 125·89 for iodine ($H=1$); when the same silver iodide is further purified by Ladenburg's method, the value for the atomic weight as a mean of eight determinations becomes 125·984, a value much nearer that obtained by Ladenburg (126·008) than to Stas' value (125·90). The treatment of the iodide with ammonia thus effects a real purification. The author has also prepared hydrogen iodide from carefully purified ethyl iodide, which, on account of the great difference in the boiling points of the ethyl haloids should be free from chlorine or bromine; the value for the atomic weight of iodine obtained by converting the hydriodic acid into silver iodide was found to be 126·026. Finally, the combustion of silver in a current of iodine gave a value for iodine 126·011 ($H=1$).
W. A. D.

Autoxidation of Sulphur. AUGUST HARPF (*Zeit. anorg. Chem.*, 1904, 39, 387—388).—Finely-divided sulphur suffers a slight oxidation on exposure to sunlight for several days in an exsiccator containing sodium hydroxide. The autoxidation of sulphur also takes place in the dark and increases with elevation of temperature. The assumption made by Windisch and others that the disinfecting property of sulphur on the moulds, formed during the growth of grapes, is due to the formation of sulphur dioxide, produced by the action on the sulphur of active oxygen and hydrogen peroxide generated by the living plants, is thus unnecessary.
A. McK.

Electrochemical Preparation of Salts of Hyposulphurous Acid. KARL ELBS and K. BECKER (*Zeit. Elektrochem.*, 1904, 10, 361—364).—Sodium hydrogen sulphite solution is electrolysed with a porous diaphragm and a cathode of platinum, aluminium, or zinc. At first, sodium hyposulphite is formed at the cathode in almost theoretical quantity, but the yield very soon falls off owing to the further reduction of the hyposulphite to thiosulphate, $Na_2S_2O_4 + 2H = H_2O + Na_2S_2O_3$. It was impossible to prepare solid sodium hyposulphite in this way. When solutions of calcium or magnesium hydrogen sulphite in water or dilute alcohol are electrolysed in the same way, a little hyposulphite is formed in solution, but the solid substance which separates out is the neutral sulphite of calcium or magnesium. Zinc hydrogen sulphite gave similar results. From a concentrated solution of sodium and zinc hydrogen sulphites, however, a solid substance is deposited, about one-quarter of which consists of sodium hyposulphite. Solutions of sodium magnesium and of sodium manganese hydrogen sulphites gave no solid substance.
T. E.

Atomic Weight of Nitrogen; Analysis by Weighing Nitrogen Monoxide. PHILIPPE A. GUYE and STEFAN BOGDAN (*Compt. rend.*, 1904, 138, 1494—1496).—The discrepancy between the values for the atomic weight of nitrogen as determined by Stas (14.04 to 14.05 according to the method of calculation), and deduced from physico-chemical methods by Guye (14.004; compare this vol., ii, 392, 475), has led the authors to make a new determination of the value, using a direct method. The method consisted in decomposing a known weight of nitrogen monoxide by means of a spiral of iron wire raised to incandescence by an electric current; the difference between the weight of the wire before and after the experiment gave the weight of the oxygen contained in the known weight of nitrogen monoxide, from which the atomic weight of nitrogen in the system $O=16$ was obtained. The mean of six determinations was 14.007, with an upper and lower limit of 14.023 and 13.992 respectively. The authors do not consider the result conclusive, but the close approximation of this value to the one deduced from physico-chemical methods justifies in their opinion a revision of the value $N=14.04$ adopted by the International Commission for Atomic Weights in the table for 1904. M. A. W.

Determination of the Atomic Weight of Nitrogen by the Volumetric Analysis of Nitrogen Monoxide. ADRIEN JAQUEROD and STEFAN BOGDAN (*Compt. rend.*, 1904, 139, 49—51. Compare preceding abstract).—The authors have determined the atomic weight of nitrogen by a volumetric method which consists in decomposing nitrogen monoxide in a constant volume apparatus by means of a spiral of iron wire heated to redness by an electric current; owing to a difference in the compressibility of the two gases, an additional pressure of about 5 mm. is necessary to bring the residual nitrogen to the same volume as the original nitrogen monoxide. Knowing this increase of pressure, the initial pressure, and the densities of nitrogen monoxide and of nitrogen, the atomic weight of nitrogen can be calculated from the ratio N_2/N_2O .

The nitrogen monoxide was prepared by the action of sodium nitrite on hydroxylamine sulphate, the measurements made at 0° and the pressures approximating to 760 mm. were read to 1/100 mm.; using the values obtained by Rayleigh and Leduc for the weight of a normal litre of nitrogen and of nitrogen monoxide, the atomic weight of nitrogen deduced from these experiments is 14.019 ($O=16$).

M. A. W.

Solubility of Nitrogen in Liquid Oxygen. ERNST ERDMANN and FRED BEDFORD (*Ber.*, 1904, 37, 2545—2550. Compare this vol., ii, 328).—A reply to Stock's criticisms (this vol., ii, 396). It is shown experimentally that when nitrogen gas is passed into pure liquid oxygen the boiling point of the latter is lowered to a much greater extent than when gaseous oxygen is passed into the same liquid; the lowering of the boiling point is continuous to a certain extent, thus, after two minutes, it is 0.99, after 5 minutes 1.26, and after 12 minutes 1.94. When gaseous hydrogen is passed instead of nitrogen, the fall in boiling point is greater (2.9°), and takes place suddenly. After

passing nitrogen gas, the residual liquid is no longer pure oxygen, but contains from 2 to 10 per cent. of nitrogen, showing that liquid oxygen at its boiling point absorbs nitrogen. W. A. D.

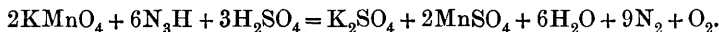
Hydronitric Acid [Azoimide] and the Inorganic Trinitrides. LOUIS M. DENNIS and A. W. BROWNE (*J. Amer. Chem. Soc.*, 1904, 26, 577—612).—A *résumé* is given of previous work on azoimide and the inorganic trinitrides (azoimides).

The azoimide used in the present investigation was prepared by a modification of Wislicenus' method (Abstr., 1892, 1151), which depends on the action of nitrous oxide on heated sodamide. The process was carefully studied and is described in detail.

Lithium and barium azoimides crystallise from aqueous solutions with H_2O , but when these salts are left over sulphuric acid in a desiccator they gradually become anhydrous. Silver azoimide is soluble in boiling water to the extent of about 0.1 gram per litre.

It has been shown by Curtius and Darapsky (Abstr., 1900, ii, 474) that when sodium azoimide is treated with solution of iron alum or ferric chloride, a deep red coloration is produced. This test is found to be very delicate and of general application to the inorganic trinitrides. The colour is discharged by the addition of dilute hydrochloric acid, whilst the colour of ferric thiocyanate is not affected by this reagent. Mercuric chloride, however, discharges the colour of ferric thiocyanate more readily than it does that of ferric azoimide. By means of these reactions, trinitrides and thiocyanates may be detected in presence of each other.

The estimation of azoimide cannot be satisfactorily effected by titration with potassium permanganate in presence of sulphuric acid, since the reaction takes place very slowly towards the end, and it is therefore impossible to secure a definite end-point, and also because the substances tend to react in somewhat different proportions under varying conditions. The reaction probably takes place in accordance with the following equation :



E. G.

Properties of Mixtures of Nitric and Sulphuric Acids. II. A. V. SAPOSCHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 518—532. Compare Abstr., 1904, ii, 251).—Analysis of the vapour obtained from all mixtures of nitric and sulphuric acids containing from 100 to 30 per cent. of nitric acid shows that it consists of the pure monohydrate, HNO_3 ; with less nitric acid in the mixture, the vapour contains a larger proportion of nitrogen than the monohydrate, owing to the formation of nitrogen pentoxide by dehydration. The action of sulphuric acid on nitric acid containing water is hence to absorb the water and concentrate the nitric acid, thus rendering the nitrating action of the mixture more vigorous. The composition of the mixture possessing the highest vapour pressure is almost exactly expressed by : $5\text{HNO}_3 + 2\text{H}_2\text{SO}_4 + 3\text{H}_2\text{O}$. T. H. P.

Acid Nitrates. ERICH GROSCHUFF (*Zeit. anorg. Chem.*, 1904, 40, 1—23).—Ammonium trinitrate, $\text{NH}_4\text{NO}_3 \cdot 2\text{HNO}_3$, prepared by dissolving ammonium nitrate in nitric acid of sp. gr. 1.514 at 20° and then allowing the solution to crystallise at 0° , separates in needles or prisms and melts at $29\text{--}30^\circ$, whilst Ditte gives 18° . It is a stable salt, differing from the labile *ammonium dinitrate*, $\text{NH}_4\text{NO}_3 \cdot \text{HNO}_3$, prepared by dissolving ammonium nitrate (1 mol.) in nitric acid (1 mol.), cooling the mixture first quickly to 10° , and then to a temperature not exceeding 6° ; when the separation of the salt begins, the temperature rises to its melting point, namely, 11.5° . A stable eutectic mixture of trinitrate and normal salt (m. p. 16°) of almost the same composition as the dinitrate may also be formed. The solubility of ammonium nitrate in nitric acid was determined. The dinitrate is decomposed by water, but the trinitrate is not.

Potassium trinitrate, $\text{KNO}_3 \cdot 2\text{HNO}_3$, melts at 22° and not at -3° , as quoted by Ditte; it crystallises in prisms. *Potassium dinitrate*, $\text{KNO}_3 \cdot \text{HNO}_3$, is stable only between $21\text{--}22^\circ$ (its eutectic point with the trinitrate) and $28\text{--}29^\circ$ (the transition temperature into the normal salt); it crystallises in leaflets. The trinitrate forms with normal potassium nitrate a eutectic mixture which melts at 21° .

The ammonium nitrates described, with the exception of the trinitrate, are more soluble in nitric acid than are the corresponding potassium salts. The saturated solutions of the two trinitrates and ammonium dinitrate are richer in nitric acid than are the corresponding solid phases.

The dinitrates are decomposed by water. Potassium trinitrate first dissolves without decomposition at temperatures between -1° and 22° , then normal salt separates. The solubility of potassium mononitrate in water first falls on the addition of nitric acid and then rises.

A. McK.

Action of Gaseous Ammonia on Arsenic Trichloride, Tribromide, or Tri-iodide. CHARLES HUGOT (*Compt. rend.*, 1904, 139, 54—56).—By the action of ammonia on arsenic trichloride, tribromide, or tri-iodide at -30° to -40° in a special apparatus previously described (compare Abstr., 1901, ii, 18), *arsenamide* is formed together with ammonium chloride, bromide, or iodide according to the equation $\text{AsCl}_3 + 6\text{NH}_3 = \text{As}(\text{NH}_2)_3 + 3\text{NH}_4\text{Cl}$. Arsenamide is a greyish-white, amorphous powder, insoluble in liquid ammonia, stable below 0° when out of contact with moist air, and at the ordinary temperature in an atmosphere of ammonia; it is decomposed by water to form arsenious oxide and ammonia, and at temperatures above 0° decomposes slowly into *arsenamide* according to the equation $2\text{As}(\text{NH}_2)_3 = \text{As}_2(\text{NH})_3 + 3\text{NH}_3$; the decomposition is complete at 60° , and the imide is a stable, yellow, amorphous compound, which is not decomposed when heated at 100° in a vacuum and is less readily decomposed by water than the amide; when heated at 250° , however, it loses ammonia and is converted into *arsenic nitride*, $\text{As}_2(\text{NH})_3 = 2\text{AsN} + \text{NH}_3$, which is an orange-red solid decomposing into arsenic and nitrogen at a temperature not far removed from its point of formation.

M. A. W.

Non-existence of Arsenic Pentachloride. WARREN RUFUS SMITH and JOSEPH E. HORA (*J. Amer. Chem. Soc.*, 1904, 26, 632—635).—By the action of chlorine on arsenic trichloride at -34° , Baskerville and Bennett (*Abstr.*, 1903, ii, 208) obtained a substance which they assumed to be arsenic pentachloride.

It has been found that the freezing point of a solution of chlorine in arsenic trichloride in which $\text{As}:\text{Cl}=1:3$ is -16.2° and that the freezing point falls regularly as the proportion of chlorine increases, that of a solution in which $\text{As}:\text{Cl}=1:9$ being -59.5° . When a solution containing molecular proportions of chlorine and arsenic trichloride is cooled, solid begins to separate at -48° , but the substance does not solidify completely, some liquid still remaining at -70° . The solid substance which separates seems in every case to be arsenic trichloride; it is therefore concluded that arsenic pentachloride is not formed under these conditions, and that the product described by Baskerville and Bennett was merely a solution of chlorine in arsenic trichloride.

E. G.

Solubility of Silicon in Silver. A Crystalline Variety of Silicon Soluble in Hydrofluoric Acid. HENRI MOISSAN and F. SIEMENS (*Compt. rend.*, 1904, 138, 1299—1303).—Silicon is much more readily soluble in silver than in either lead or zinc (compare this vol., ii, 332), 100 parts of silver dissolving 9.22 parts at 970° , 14.89 at 1150° , 19.26 at 1250° , and 41.46 at 1470° . The silicon recovered from the solution is a mixture of ordinary crystalline silicon and a new allotropic crystalline form which is soluble in hydrofluoric acid and has a sp. gr. of 2.42 in benzene. The yield of the new allotropic modification appears to be independent of the temperature at which the solution has been effected and of the velocity of cooling, but decreases as the amount of silicon in the original solution increases, being 58.02, 27.60, 19.00, and 16.00 per cent. respectively in the four mixtures given above, and 99 per cent. in a 2 per cent. solution of silicon in silver. The new variety is unchanged by heating at 1200° in hydrogen or nitrogen, and contains only slight traces of iron and silicon carbide as impurities.

M. A. W.

Coagulation of Colloidal Silver. A. W. DUMANSKY (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 465—468).—As regards their action on colloidal solutions of silver prepared by Carey Lea's method, metallic salts may be divided into two groups: (1) salts of oxides of metals of which sub-oxides also exist, such as mercuric chloride, cupric chloride, ferric chloride, &c.; these change into salts of the sub-oxides. (2) This comprises salts of oxides to which no sub-oxides correspond and also salts of sub-oxides. Such salts either reduce the silver to metal or coagulate it, losing part of their acid, or do not undergo change, but precipitate the silver, as happens with salts of ferrous oxide.

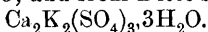
T. H. P.

Reactivity of Calcium Sulphate in Colloidal Media. PAUL ROHLAND (*Zeit. anorg. Chem.*, 1904, 40, 182—184).—The hardening of calcium sulphate is possibly due to the formation of a dilute, solid

solution of the water (of crystallisation, constitution, or dilution) with the calcium sulphate.

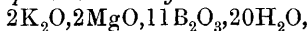
A. McK.

Formation of Oceanic Salt Deposits. XXXVII. Potassium Pentacalcium Sulphate and a Double Compound analogous to Kaliborite. JACOBUS H. VAN'T HOFF [in part with GEIGER and LICHTENSTEIN] (*Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 28, 935—937).—*Potassium pentacalcium sulphate*, $K_2Ca_5(SO_4)_6$, prepared by heating precipitated gypsum for from one to three days with a 5 per cent. solution of potassium sulphate until microscopic examination shows that all the gypsum has been converted into the double salt, is distinct from syngenite, $CaK_2(SO_4)_2 \cdot H_2O$, and from Ditte's double salt,



The ratio between the number of molecules of potassium sulphate and 1000 molecules of water was determined at 83° for saturated solutions of (a) potassium sulphate, (b) potassium sulphate and syngenite, (c) syngenite and potassium pentacalcium sulphate, and (d) potassium pentacalcium sulphate and anhydrite respectively. For the preparation of potassium pentacalcium sulphate at 83° , a solution of potassium sulphate, containing 5.6 molecules to 1000 molecules of water, is most suitable.

The preparation of *potassium magnesium borate*,



from pinnoite, potassium chloride, and boric acid, is also described.

A. McK.

Decomposition of Mixtures of Calcium Carbonate and an Alkali Carbonate under the Action of Heat in a Vacuum. PAUL LEBEAU (*Compt. rend.*, 1904, 138, 1496—1498. Compare Abstr., 1903, ii, 477; this vol., ii, 121).—The experiments described in this paper were undertaken with the object of studying the action of the alkali oxides on calcium oxide at a high temperature. Preliminary experiments (compare this vol., ii, 121) having shown that the alkali carbonates are readily dissociated into carbon dioxide and the alkali oxide at a high temperature and under reduced pressure, molecular mixtures of calcium carbonate and an alkali carbonate (caesium, rubidium, sodium, or potassium) were heated in a vacuum; decomposition was complete at about 1000° , carbon dioxide equivalent to the carbonate taken was evolved, and the residue consisted of pure lime in the form of transparent skeleton crystals, prismatic in the case of the mixtures containing caesium and rubidium and lamellar in the case of the mixtures containing sodium or potassium; these crystalline fragments are without action on polarised light, and resemble the crystalline or fused lime obtained by Moissan in being much less readily attacked by reagents than ordinary lime; for example, they retain their transparency in water, and only become superficially hydrated after prolonged contact.

The dissociation of the mixed carbonates proceeds much less readily than that of calcium carbonate alone, and the dissociation pressure is always lower than that of pure calcium carbonate and higher than that of the pure alkali carbonate for the same tempera-

ture; thus the decomposition of the mixture containing caesium carbonate began at 540° , and at 1020° the dissociation pressure was 490 mm.; that of pure calcium carbonate would be greater than one atmosphere. These facts point to the existence of double carbonates of calcium and the alkali metal possessing different dissociation pressures.

M. A. W.

Electrolytic Preparation of Magnesium and Zinc Peroxides. FRIEDRICH HINZ (D.R.-P. 151129).—Preparations of magnesium and zinc peroxides, obtained by chemical means, contain a considerable proportion of lower oxides. Better products are obtained by electrolysing solutions of zinc or magnesium chloride in vessels having a porous diaphragm, hydrogen peroxide being added to the solution in the cathode-cell. Platinum or carbon anodes and platinum or tin cathodes are employed. The concentrated solution of the metallic salt is first neutralised by adding the corresponding oxide and then electrolysed, magnesium requiring a potential difference of 6–7 volts and zinc 2.5–3 volts. The precipitated hydrated peroxides are collected and dried, special precautions being taken to avoid decomposition. The reaction takes place according to the equation $\text{Mg} + \text{H}_2\text{O}_2 + 2\text{H}_2\text{O} = \text{Mg}(\text{OH})_4$. The magnesium peroxide obtained contains 40–50 per cent. of MgO_2 , and the zinc peroxide 55–60 per cent. of ZnO_2 , the theoretical values being 60 and 73 per cent. respectively.

C. H. D.

Preparation and Electrolysis of Pure Molten Zinc Chloride. SIEGFRIED GRÜNAUER (*Zeit. anorg. Chem.*, 1904, 39, 389–476).—When commercial zinc chloride is heated until the evolution of steam is no longer perceptible and then electrolysed, either in a crucible over a free flame or in a U-tube, hydrogen is evolved at the cathode, the amount of hydrogen gradually diminishing until finally only zinc separates. As various specimens of commercial zinc chloride exhibit different behaviour on being electrolysed, the author has studied the conditions for the preparation of pure zinc chloride. The experimental conditions under which the various specimens of zinc chloride were electrolysed are very fully described. Those specimens which were readily electrolysed were found to contain ammonium chloride, and the influence of ammonium chloride on specimens of zinc chloride, which suffered electrolysis with difficulty, was accordingly investigated. In none of the latter cases did the separation of zinc take place at once. Experiments were next conducted with mixtures of zinc chloride and ammonium chloride in varying proportions, the mixtures having been dehydrated at 260° as far as possible. Another set of experiments is described where the mixtures were dehydrated with dry hydrogen chloride. With increasing amounts of ammonium chloride, the electrolysis proceeds with less ease; the molten masses remain free from zinc dust, but the preliminary evolution of gas at the cathode persists for a long time. The most favourable result was obtained with a mixture in the proportion of 11 mols. of zinc chloride to 1 mol. of ammonium chloride. The gases evolved at the anode were chlorine, hydrogen chloride, oxygen (resulting from the moisture still

retained by the fused ammonium chloride), carbon monoxide or carbon dioxide (resulting from the oxidation of the carbon poles), and nitrogen (resulting from the oxidation of ammonium chloride by chlorine), whilst hydrogen, ammonia, and nitrogen were evolved at the cathode. The amounts of these gases were determined by gasometric methods.

Anhydrous zinc chloride is prepared by heating ordinary zinc chloride, which has been dehydrated as far as possible, with concentrated hydrochloric acid. It may also be prepared by passing dry chlorine into fused zinc or by adding zinc to molten lead chloride. An apparatus is described by means of which zinc chloride was dehydrated by a stream of hydrogen chloride.

The electrolysis of pure zinc chloride was next studied under varying conditions of current strength. A description of the separation of iron and zinc by the fractional electrolysis of their fused chlorides is given. Mixtures of zinc chloride with potassium and sodium chlorides respectively were also electrolysed with varying current strengths. The metallic cloud, which separates during the electrolysis of zinc chloride at the initial stage, has a lustre like that of mercury. A. McK.

Metallic Hydroxides. I. H. W. FISCHER (*Zeit. anorg. Chem.*, 1904, 40, 39—53).—The solubility of copper hydroxide in sodium hydroxide solution falls as the latter becomes more dilute. When copper nitrate was used instead of copper sulphate in the preparation of copper hydroxide, the solubility of the latter in sodium hydroxide did not increase. The influence of sodium and potassium carbonates respectively on the solubility of copper hydroxide in sodium hydroxide is slight.

The solubility of chromium hydroxide in an aqueous solution of red chromic chloride is not directly proportional to the concentration of the latter. A basic chloride is probably formed. From a solution of chromium hydroxide in aqueous chromic chloride, the former cannot be precipitated either by the addition of electrolytes or by the action of heat; part of it is supposed to be in solution in the colloidal form and part in the form of a compound containing chlorine.

Determinations of the solubility of aluminium hydroxide in aluminium chloride solution show that a portion of the former goes into solution to form a compound, whilst part is in the colloidal form. The colloidal portion existing in such solutions was precipitated by barium sulphate, and the concentration of the hydrogen ions before and after the addition of barium sulphate was determined by the methyl acetate method. A. McK.

Basic Mercury Salts. ALVIN J. COX (*Zeit. anorg. Chem.*, 1904, 40, 146—181).—The hydrolysis of the mercury salts, HgCrO_4 , $\text{Hg}(\text{NO}_3)_2$, HgSO_4 , HgNO_3 , Hg_2SO_3 , causes the formation, first of all, of basic salts and then of the oxide. Mercuric fluoride, HgF_2 , is hydrolysed directly to mercuric oxide and hydrogen fluoride. The basic salts obtained were $3\text{HgO}, \text{CrO}_3$; $3\text{HgO}, \text{N}_2\text{O}_5$; $3\text{HgO}, \text{SO}_3$; $5\text{Hg}_2\text{O}, 3\text{N}_2\text{O}_5, 2\text{H}_2\text{O}$; $2\text{Hg}_2\text{O}, \text{SO}_3, \text{H}_2\text{O}$. In accordance with the Phase Rule, the single salts require a minimum concentration of the hydrolytically dissociated acid, the determination of which renders the

preparation of the pure basic salts possible. The basic salts quoted are intermediate between normal salts and oxides; other basic salts, quoted in the literature, are simply mixtures of two individuals in undefined proportions.

The hydrolysis of mercuric salts is considerably greater than that of mercurous salts, which also accords with the difference in electro-affinity of the two cations. The hydrolysis of mercurous nitrate is more complicated than that of mercuric nitrate. A. McK.

Bismuth-aluminium and Magnesium-aluminium Alloys. HECTOR PÉCHEUX (*Compt. rend.*, 1904, 138, 1501—1503. Compare this vol., ii, 404).—I. *Bismuth-aluminium* alloys. Attempts to prepare alloys containing less than 70 per cent. of aluminium were unsuccessful, the ingot consisting of three layers, the lower one being heterogeneous and containing bismuth in excess, the middle one being an alloy containing about 70 per cent. of aluminium, whilst the upper one was a homogeneous alloy containing about 90 per cent. of aluminium. Alloys containing 75, 85, 88, and 94 per cent. of aluminium with the sp. gr. of 2·857, 2·79, 2·776, and 2·74 at 20° respectively have melting points intermediate between those of the two component metals; they are sonorous, brittle, and have a beautiful silvery-white colour. They are stable in dry or moist air, readily attacked by concentrated or dilute acids, hot or cold, and by potassium hydroxide in the cold, and decompose distilled water at 18° or 95° into hydrogen and oxygen (compare this vol., ii, 487), the bismuth becoming slightly oxidised; this reaction is probably due to a thermochemical action induced by the unequal heating of the two metals in the process of filing.

II. *Magnesium-aluminium* alloys. Alloys containing 66, 68, 73, 77, and 85 per cent. of aluminium with the sp. gr. of 2·244, 2·275, 2·324, 2·373, and 2·474 at 21° respectively have melting points not far removed from that of aluminium, are brittle, have a beautiful silvery-white colour, and are capable of taking a good polish. They are stable in the air at the ordinary temperature, but burn readily at a red heat, are readily attacked by concentrated or dilute acids, hot or cold, with the exception of the alloys containing 85, 77, and 73 per cent. of aluminium, which are not attacked by dilute sulphuric acid, and are readily attacked by potassium hydroxide solution in the cold. Hydrogen peroxide is decomposed by these alloys, the magnesium suffering oxidation, and they decompose water. M. A. W.

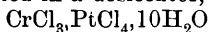
Aluminium Chlorate: its Hydrates and its Decomposition on Heating. DMITRI K. DOBROSERDOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 468—483).—Aluminium chlorate, prepared by the interaction of barium chlorate and aluminium sulphate, is deposited from its solutions, on evaporation over sulphuric acid, in the form of the two hydrates, $\text{Al}(\text{ClO}_3)_3 \cdot 9\text{H}_2\text{O}$ (in the cold) and $\text{Al}(\text{ClO}_3)_3 \cdot 6\text{H}_2\text{O}$ (when hot). These hydrates correspond with Flavitsky's theoretical chemical types of a monohydro-ortho-acid, $\text{RH}(\text{OH})_6 = \text{RHO}_3 \cdot 3\text{H}_2\text{O}$, and its first anhydride. The salt cannot be obtained in the anhydrous state owing to its ready decomposability.

Aluminium chlorate undergoes decomposition in two ways: (1) on being slowly and cautiously heated (at 100°), it explodes, owing to the evolution of chlorine dioxide, which detonates, and (2) when rapidly and energetically heated, it does not explode, but evolves chlorine, the basic chlorate, $\text{Al}_2(\text{ClO}_4)_6$, Al_2O_3 , being probably left in the residue. T. H. P.

A Basic Ferric Phosphite. E. BERGER (*Compt. rend.*, 1904, 138, 1500—1501).—The white substance obtained by Grützner (compare Abstr., 1898, ii, 216) by dissolving recently precipitated ferric hydroxide in phosphorus acid and precipitating with excess of water has a variable composition intermediate between that of an acid and a neutral phosphite; if, however, the precipitate is washed with cold water to remove all traces of free phosphorus acid and then dried, the resulting white powder has a constant composition, and is found to be a *basic ferric phosphite*, $\text{Fe}_4(\text{HPO}_3)_6$, $\text{Fe}(\text{OH})_3$, $5\text{H}_2\text{O}$. M. A. W.

Separation of Nickel and Cobalt. HANS ALBERT FRASCH (D.R.-P. 151955. Compare this vol., ii, 128).—Nickel and cobalt may be separated by precipitating a strongly ammoniacal solution of their salts by means of an alkali chloride, filtering off the precipitate, and washing with water. Nickel ammonio-chloride passes into solution, cobalt ammonio-chloride is decomposed according to the equation: $\text{Co}(\text{NH}_3)_2\text{Cl}_2 + 4\text{NH}_3 + 2\text{H}_2\text{O} = \text{Co}(\text{OH})_2 + 2\text{NH}_4\text{Cl} + 4\text{NH}_3$. For electrolytic purposes, the cobalt hydroxide thus obtained may be dissolved in ammonia, reprecipitated by alkali chloride, and again dissolved in ammonia. C. H. D.

Certain Compounds of Chromium. GEORGE O. HIGLEY (*J. Amer. Chem. Soc.*, 1904, 26, 613—632).—When platinum chloride is added to a solution of green chromic chloride, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, and the product is slowly evaporated in a desiccator, the *compound*



separates in thin, rhombic plates. On treating a solution of this salt with silver nitrate, silver platinumchloride is precipitated together with a trace of silver chloride. From further experiments, it was concluded that the platinum compound is a derivative of a hypothetical chromic chloride, $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2$, with doubled water molecules in the complex and its formula is $\{\text{CrCl}[(\text{H}_2\text{O})_2]_5\} \text{PtCl}_6$.

When violet chromium chloride, $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$, is heated at 65 — 70° , it is gradually converted into the ordinary green salt. Various attempts were made to prepare the green chloride described by Peligot (*Compt. rend.*, 1844, 19, 738) in which two-thirds of the chlorine is immediately precipitated in the cold by solution of a silver salt, but without success.

The green chloride, $\text{CrCl}_2[(\text{H}_2\text{O})_2]_4(\text{H}_2\text{O})_2\text{Cl}$, dissolves in water without development or absorption of heat. The heat of solution of the ordinary green chloride, $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl}(\text{H}_2\text{O})_2$, was found by Recoura to be -0.04 K. It is evident, therefore, that the doubling of the water molecules of the complex has only a slight effect on the heat of solution. The heat of solution of the chloride, $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl}$, is

83.96 K ; this value therefore represents the amount of heat developed on the addition of 2 gram-mols. of water to 1 gram-mol. of the green salt containing $4\text{H}_2\text{O}$.

Methods are described for the preparation of violet chromic sulphate and violet chromic iodide. The latter salt forms deep violet crystals, but, when powdered, is of an olive-green colour ; it appears to contain three doubled water molecules in its complex, and is represented by the formula $\{\text{Cr}[(\text{H}_2\text{O})_2]_3\}\text{I}_3$.

Zinc chromium fluoride, $[\text{Zn}(\text{H}_2\text{O})_6](\text{CrF}_5\cdot\text{H}_2\text{O})$, and *copper chromium fluoride*, $[\text{Cr}(\text{H}_2\text{O})\text{F}_5][\text{Cu}(\text{H}_2\text{O})_4]$, were prepared and analysed.

By dissolving freshly precipitated chromic hydroxide in glacial acetic acid, Recoura obtained a salt to which he assigned the formula $\text{Cr}(\text{H}_2\text{O})_5(\text{C}_2\text{H}_3\text{O}_2)_3$. It is considered probable that this substance was not the normal salt, since it was amorphous and contained only 5 mols. instead of 6 mols. H_2O . An attempt to prepare a crystalline normal salt was made by evaporating the solution at 0° , when a small quantity of bluish-violet crystals was obtained. Analysis of this substance indicated that it contained 6 mols. H_2O , but the salt had evidently lost acetic acid, and the result was therefore inconclusive. Further attempts were made to prepare this salt in quantity, but without success.

E. G.

Reactions of Uranous and Manganous Salts. WILLIAM ECHSNER DE CONINCK (*Bull. Acad. Roy. Belg.*, 1904, 360—362).—When nitric acid is added to hot aqueous solutions of uranous or manganous sulphates, alone or in presence of sulphuric acid, no evolution of nitric oxide occurs. A neutral aqueous solution of manganous chloride behaves similarly with nitric acid, but in presence of sulphuric acid the liquid becomes brown and there is a rapid evolution of chlorine and nitrous vapours. It is suggested that the momentary darkening of the liquid may be due to the formation of manganese tetrachloride.

T. A. H.

Uranium Oxides and Carbonate. WILLIAM ECHSNER DE CONINCK (*Bull. Acad. Roy. Belg.*, 1904, 363—365 and 448—449. Compare Abstr., 1901, ii, 165).—It is suggested that the red oxide of uranium already described has the formula $(\text{UO}_3)_2$, and is a polymeride of the orange-coloured oxide. The polymeride combines with acetic acid, so that cryoscopic measurements in this solvent gave no definite results.

When green uranium oxide is dissolved in sulphuric or hydrochloric acid and to the liquid, previously diluted with three times its volume of water, a strong aqueous solution of methylamine is added, a brown, flocculent precipitate is formed, which is readily soluble in dilute acids. When washed with water during a day and then warmed in water for several hours, it becomes pulverulent, very dense, and difficultly soluble in acids, and cryoscopic measurements indicate that it has undergone polymerisation.

When aqueous solutions of potassium carbonate and uranium nitrate are mixed, the yellow precipitate obtained appears to consist of a mixture of uranium carbonate with potassium uranyl carbonate.

On ignition, it furnishes potassium uranate and the hydrated oxide, $\text{UO}_3 \cdot \text{H}_2\text{O}$. When the precipitate is washed with water, it is converted into a mixture of uranium carbonate and uranic oxides, and the wash-water on evaporation leaves a residue containing the hydrated oxide, $\text{UO}_3 \cdot \text{H}_2\text{O}$, and potassium uranyl carbonate, but no potassium uranate.

T. A. H.

Influence of Pressure on the Melting Point of Tin and of Bismuth. GUSTAV TAMMANN (*Zeit. anorg. Chem.*, 1904, 40, 54—60).—The influence of pressure on the melting point of tin and of bismuth was studied. The metal was fused in an electric oven and the curve of cooling determined at different pressures by means of a thermoelement. Increase of pressure raises the melting point in the case of tin, and lowers it in the case of bismuth. In the apparatus described, temperatures up to 400° and pressures up to 3000 kilos. per square cm. could be registered. With bismuth, the change of the temperature of the melting point is represented by $\Delta t = -0.00386 (p - 1)$, and with tin by $\Delta t = +0.00216 (p - 1)$, where p = pressure in kilos. per square cm.

A. McK.

Physico-chemical Researches on Tin. V. ERNST COHEN (*Zeit. physikal. Chem.*, 1904, 48, 243—245. Compare Abstr., 1900, ii, 83, 212, 408; 1901, ii, 106, 244).—A remarkable case of tin corrosion at Ohlau (Schlesien) is recorded and illustrated by photographs.

J. C. P.

Stannichlorides of the Types M_2SnCl_6 and $\text{M}''\text{SnCl}_6$. I. EUGEN VON BIRON (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 489—518).—The author has prepared and analysed a number of stannichlorides, of which Rb_2SnCl_6 , $\text{ZnSnCl}_6 \cdot 6\text{H}_2\text{O}$, $\text{FeSnCl}_6 \cdot 6\text{H}_2\text{O}$, and $\text{SrSnCl}_6 \cdot 4\text{H}_2\text{O}$ have not been previously described. The compound of Li_2SnCl_6 with $8\text{H}_2\text{O}$ (Chassevant, *Ann. Chim. Phys.*, 1893, [vi], 30, 124) could not be obtained, but only the hexa-hydrated salt. No double compounds of stannic chloride with BaCl_2 , CdCl_2 , CuCl_2 , AgCl , PbCl_2 , or TlCl could be prepared.

The stannichlorides are completely analogous to the platinichlorides. Calcium stannichloride and platinichloride occupy intermediate positions between the corresponding salts of the metals of the magnesium group (Mg, Zn, Cd, Mn, Fe, Co, Ni, and Cu) and those of the glucinum group (Gl, Sr, Ba).

Chlorostannic acid is considerably less stable than chloroplatinic acid, and the same holds for the corresponding complexes of the stannichlorides and platinichlorides.

On investigating the equilibrium between $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoSnCl}_6 \cdot 6\text{H}_2\text{O}$, and $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and their solutions, it was found that at 20° $\text{CoSnCl}_6 \cdot 6\text{H}_2\text{O}$ separates without admixture of its components from solutions containing not less than 1.9 and not more than 5.5 mols. of SnCl_4 per mol. of CoCl_2 .

Wells' classification of double salts (Abstr., 1902, ii, 11) does not apply to the stannichlorides, since such compounds of metals which

are very similar in all their properties (K, Na, and Li; Co and Ni) are found to belong to different groups, according to this classification. Whether a double salt belongs to one or another of Wells' groups depends not only on the degree of dissociation of the salt in solution, but also on the relative solubilities of the salt and its components.

T. H. P.

Basic Zirconium Sulphate. OTTO HAUSER (*Ber.*, 1904, 37, 2024—2026).—No sparingly soluble crystalline compound of zirconium has yet been described, and this has greatly retarded the work of separating purified derivatives of the element. A systematic investigation of the basic salts has shown that the *basic sulphate*, $4\text{ZrO}_2 \cdot 3\text{SO}_3 \cdot 14\text{H}_2\text{O}$, satisfies the required conditions.

T. M. L.

Formation of Vanadium Ores in Nature. ALFRED DITTE (*Compt. rend.*, 1904, 138, 1303—1308).—Vanadium is widely though sparsely diffused throughout the earth's crust; water charged with atmospheric gases is capable of absorbing the vanadium, probably in the form of vanadic acid or soluble alkali vanadates; these waters, coming in contact with the natural ores of lead, galena, anglesite or cerusite, exert a solvent action on them, and form lead vanadate, which is the chief natural source of the element.

Experiments on the action of solutions of alkali vanadates on lead sulphate, either solid or in dilute aqueous solution, show that an equilibrium mixture of lead vanadate and the alkali sulphate is formed, but when, as in nature, the latter is removed, the transformation of the lead sulphate to the vanadate is almost complete.

M. A. W.

Allotropic Forms of Antimony Sulphide. Heats of Formation. JOSEPH GUINCHANT and PAUL CHRÉTIEN (*Compt. rend.*, 1904, 139, 51—54).—When antimony sulphide is heated in a current of nitrogen at about 850° and the vapours rapidly condensed, a mixed sublimate is formed consisting of a lilac-coloured deposit of transparent, spherical globules and of black needles, quite different from the allotropic form obtained by Rose and by Fuchs (*Ann. Phys. Chem.*, 1834, 31, 578) under similar conditions. The red precipitated sulphide and the lilac allotropic modification are readily converted into the black sulphide, by heating either alone at 220° or with dilute hydrochloric acid at 100° , and the specific gravities at 0° of the three modifications are as follows: red precipitated sulphide, 4.120; lilac sublimate, 4.278; fused black precipitated sulphide, 4.652; synthetic black sulphide, 4.659. Using the value, 34 Cal., determined by Berthelot (*Abstr.*, 1886, 308, 512) for the heat of formation of the moist precipitated sulphide, the heats of formation of the various forms have been determined from their heats of solution in sodium sulphide solution, with the following results: for the dried precipitate, 32.6 Cal., for the lilac sublimate, 33.9 Cal., and for the black sulphide 38.2 Cal.

M. A. W.

Mixtures of Certain Sulphides and Selenides with Corresponding Metals. HENRI PÉLABON (*J. Chim. Phys.*, 1904, ii, 321—339).—By means of a thermo-electric couple, the melting point curve was traced for mixtures of bismuth or antimony with sulphur or selenium. In the case of mixtures of bismuth and sulphur containing less sulphur than the amount corresponding with BiS , the initial point of solidification varied with composition; the final was the melting point of bismuth. The curves also indicate clearly the existence of BiS and show that the compound forms a homogeneous liquid with excess of bismuth. Similar results were obtained with bismuth and selenium. Mixtures of antimony and sulphur containing antimony in excess separate, however, into two layers, the upper a solution of antimony in its sulphide, the lower a solution of the sulphide in antimony, unless the proportion of sulphur is below 1.5 per cent., when the sulphide is completely dissolved in the metallic antimony. Selenium and antimony do not, however, form two layers. The melting point curves are given in the two cases. L. M. J.

Bismuth Tetroxide OTTO HAUSER and LUDWIG VANINO (*Zeit. anorg. Chem.*, 1904, 39, 381—386).—Whilst bismuth trioxide yields a mixture of tetroxide and pentoxide on oxidation with potassium hydroxide and chlorine, it yields the tetroxide only when alkaline potassium ferricyanide is used as the oxidising agent; the action is practically quantitative when bismuth trioxide (1 mol.) is boiled with potassium ferricyanide (2 mols.) in potassium hydroxide solution. The oxide, when dried at 100° , contains $1\text{H}_2\text{O}$, and, when dried at the ordinary temperature, $2\text{H}_2\text{O}$; it becomes anhydrous at 160 — 170° . The oxide has acid characters; when heated with potassium hydroxide solution, it turns brown and appears to form a potassium salt, from which the free hydroxide may be regenerated by the addition of dilute nitric acid. No hydrogen dioxide is formed on the addition of concentrated sulphuric acid. A. McK.

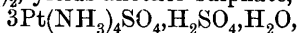
Chemical Effects of Light. Action of Hydrochloric Acid on Platinum and Gold. MARCELLIN BERTHELOT (*Compt. rend.*, 1904, 138, 1297—1299).—When pure gold or platinum foil immersed in fuming hydrochloric acid, of sp. gr. 1.178 (36 per cent.), in flasks containing air, is exposed to the action of light for four months, the metal slowly dissolves, forming the chloride, and the rate of solution is increased by the addition of a trace of manganous chloride to the solution (compare Abstr., 1890, 6). If, however, the experiment is conducted in the dark, the metal is not attacked by the acid. The action of the light appears to facilitate the fixation of free oxygen, which displaces the chlorine from the hydrogen chloride.

M. A. W.

Platinum-ammonium Compounds. HANS EULER and ASTRID EULER (*Ber.*, 1904, 37, 2391—2395).—When recrystallised from water, Grimm's red salt (*Annalen*, 1856, 99, 95) yields *chloroplatinodiammine chloride*, $\text{Pt}(\text{NH}_3)_4\text{Cl}_4$, which crystallises in reddish-yellow scales or as a yellow powder. It loses 2Cl on treatment with silver

nitrate, and is reduced to platodiammine chloride by hydrogen sulphide. With sulphuric acid, the chloride yields *chloroplatinodiammine sulphate*, which crystallises in flat, red needles, becomes white and opaque on contact with water, and regains its red colour on addition of hot concentrated sulphuric acid. The action of ammonia on chloroplatinous acid leads to the formation of diplatosemidiammine chloride, $\text{Pt}_2(\text{NH}_3)_4\text{Cl}_2$, and platosemidiammine chloride, $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$. The filtrate from these gives a precipitate of slender, white needles (hydroxychloroplatinodiammine chloride?) on addition of platodiammine chloride.

When recrystallised from water, the diacid sulphate of Reiset's base, $\text{Pt}(\text{NH}_3)_4(\text{HSO}_4)_2$, yields another sulphate,



which crystallises in prisms and loses H_2O at 100° . In solution, the free base has the constitution $\text{Pt}(\text{NH}_3)_2(\text{NH}_3 \cdot \text{OH})_2$. G. Y.

Mineralogical Chemistry.

"Silajit," an Ancient Eastern Medicine. DAVID HOOPER (*J. Asiatic Soc. Bengal*, 1903, 72, 99—104).—The name "silajit" (meaning rock-sweat) is applied to a variety of substances used as drugs, which occur as exudations upon rocks in the mountainous districts of northern India. One variety consists of aluminium sulphate, another ("white silajit") of dried urine of the wild hill-goat, and a third ("black silajit") consists of an organic acid combined with alkalis. The last-named variety is almost wholly soluble in water, and has the following composition :

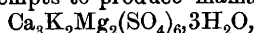
| | Water. | Organic matter. | Ash. | Total. | Nitrogen in organic matter. |
|------|--------|-----------------|-------|--------|-----------------------------|
| I. | 9.85 | 56.20 | 34.95 | 100.00 | 1.03 |
| II. | 15.90 | 49.86 | 34.24 | 100.00 | 0.82 |
| III. | 11.15 | 51.55 | 37.30 | 100.00 | 3.25 |
| IV. | 10.99 | 56.86 | 32.15 | 100.00 | 1.26 |

The ash has the composition :

| | Fe ₂ O ₃ . | Al ₂ O ₃ . | CaO. | MgO. | K ₂ O. | Na ₂ O. | P ₂ O ₅ . | SO ₃ . | Cl. | CO ₂ , &c. | SiO ₂ . |
|------|----------------------------------|----------------------------------|------|------|-------------------|--------------------|---------------------------------|-------------------|-------|-----------------------|--------------------|
| I. | 2.24 | 4.36 | 1.50 | 9.07 | 4.11 | 0.16 | 0.58 | 0.07 | 11.51 | 1.35 | |
| II. | 1.08 | 3.96 | 0.52 | 6.69 | 7.63 | 0.25 | 0.24 | 0.12 | 12.13 | 1.62 | |
| III. | 6.00 | 3.86 | 0.15 | 3.71 | 1.07 | 0.27 | 0.34 | 0.11 | 3.69 | 18.10 | |
| IV. | 4.64 | 3.88 | 1.34 | 6.10 | 0.81 | 0.20 | 0.14 | 0.06 | 4.82 | 10.15 | |

L. J. S.

Identity of Mamanite with Polyhalite. JACOBUS H. VAN'T HOFF and GERARDUS L. VOERMAN (*Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 984—986).—Attempts to produce mamanite,



artificially being unsuccessful, its existence as a mineral species appeared doubtful. The following new analysis of a carefully selected portion of the original material, from Maman in Persia, proves the identity of mamanite with polyhalite, $(\text{Ca}_2\text{K}_2\text{Mg}(\text{SO}_4)_4, 2\text{H}_2\text{O})$.

| Ca. | K. | Mg. | SO_4 | H_2O . | Total. |
|------|------|-----|---------------|------------------------|--------|
| 14.1 | 13.1 | 4.2 | 61.6 | 6.4 | 99.4 |

L. J. S.

Melanterite [and Alunogen] from Baluchistan. DAVID HOOPER (*J. Asiatic Soc. Bengal*, 1903, 72, 236—239).—At several localities in Baluchistan there is mined a mineral called “khaghhal,” which is used for dyeing; it occurs as a white efflorescence on decomposed slate. Analysis of the portions (about 40 per cent.) soluble in water gave the results under I (for material from Ladon Pass) and II (from Kil Chotok):

| | FeSO_4 . | $\text{Al}_2(\text{SO}_4)_3$. | CaSO_4 . | MgSO_4 . | K_2SO_4 . | Na_2SO_4 . | Total. |
|-----|-------------------|--------------------------------|-------------------|-------------------|---------------------------|----------------------------|--------|
| I. | 30.10 | 4.50 | 3.12 | 1.20 | 0.74 | 2.06 | 41.72 |
| II. | 27.36 | 4.02 | 3.78 | 1.50 | 0.27 | 2.86 | 39.79 |

Another mineral, known as “phulmâk” and used in Baluchistan as a mordant in dyeing, occurs as white, granular or silky masses; analysis of the portion soluble in water proves it to be alunogen, $(\text{Al}_2(\text{SO}_4)_3, 18\text{H}_2\text{O})$.

L. J. S.

Crystallised Rhodonite from S. Marcel (Valle d'Aosta). LUIGI COLOMBA (*Atti R. Accad. Torino*, 1904, 39, 664—668).—The author has obtained rhodonite in drusy masses of dark red crystals having the composition:

| SiO_2 . | MnO . | CaO . | Total. |
|------------------|----------------|----------------|--------|
| 46.71 | 47.73 | 5.41 | 99.85 |

corresponding with the formula $7\text{MnSiO}_3, \text{CaSiO}_3$. The crystals are very rich in forms, some of which have not been observed previously.

T. H. P.

Thuringite and Chamosite from Thuringia. EDWARD ROBINS ZALINSKI (*Jahrb. Min., 1904, Beil.-Bd.*, 19, 40—84).—A detailed account is given of the thuringite and chamosite from the deposits of iron-ore in the Lower Silurian of Thuringia. Analyses I and II of thuringite agree with the accepted formula $\text{H}_{18}(\text{Fe}, \text{Mg})_5(\text{Al}, \text{Fe})_8\text{Si}_6\text{O}_{41}$. Analyses III and IV of chamosite (impure owing to admixed carbonates) give the formula $\text{H}_{18}(\text{Fe}, \text{Mg})_9\text{Al}_6\text{Si}_6\text{O}_{39}$.

| | SiO_2 . | Al_2O_3 . | Fe_2O_3 . | FeO . | MgO . | CaO . | H_2O . | CO_2 . | Total. |
|------|------------------|---------------------------|---------------------------|----------------|----------------|----------------|------------------------|-----------------|--------|
| I. | 22.30 | 16.81 | 15.13 | 32.78 | 1.30 | — | 11.04 | — | 99.36 |
| II. | 21.35 | 17.70 | 11.57 | 36.81 | 3.90 | — | 8.78 | — | 100.11 |
| III. | 23.54 | 18.15 | 3.67 | 36.84 | 1.35 | 1.62 | 11.58 | not det. | 96.75 |
| IV. | 23.39 | 18.64 | 6.06 | 34.34 | 1.44 | 1.55 | 11.01 | not det. | 96.43 |

L. J. S.

Refraction of Tourmaline. CHARLES SORET (*Arch. Sci. phys. nat.*, 1904, [iv], 17, 573—588).—The paper contains the measurements of the indices of refraction, for ordinary and extraordinary rays, of a number of samples of tourmaline. The death of the author has unfortunately interrupted the work, and prevented the formulation of conclusions which he considered justified. L. M. J.

[Toke-uchi-mura and Weaver Mtn.] **Meteorites.** CARL KLEIN (*Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 978—983).—Analyses, by Lindner, are given of: I, the meteoric stone of Toke-uchi-mura, Yofugori, Tamba, Japan, and II, the compact meteoric iron of Weaver Mountain, near Wickenburg, Arizona.

| | SiO ₂ . | MgO. | FeO. | CaO. | MnO. | K ₂ O. | Na ₂ O. | Fe ₂ O ₃ . | Cr ₂ O ₃ . | NiO. |
|-----|--------------------|-------|-------|------|------|------------------------------------|--------------------|----------------------------------|----------------------------------|------|
| I. | 36·34 | 20·91 | 14·76 | 2·47 | 0·15 | 0·28 | 1·18 | 0·36 | 0·42 | 0·30 |
| | Fe. | Ni. | Co. | S. | P. | FeCr ₂ O ₄ . | Insol. | Total. | Sp. gr. | |
| I. | 16·58 | 1·82 | 0·05 | 2·75 | 0·08 | 0·95 | — | 99·40 | 3·815 | |
| II. | 80·78 | 17·92 | 0·84 | 0·15 | 0·12 | — | 0·15 | 99·96 | 7·108 | |

L. J. S.

Iodo-saline Water of Castel S. Pietro dell' Emilia. FELICE GARELLI and FELICE GORNI (*Chem. Centr.*, 1904, i, 1423—1424; from *Boll. Chim. Farm.*, 43, 233—239. Compare Vitali, *ibid.*, 39, 732).—The iodo-saline water of Castel S. Pietro dell' Emilia was found to have a sp. gr. 1·0112 at 4°. The yellow, flocculent precipitate which was formed when the water remained for a long time, contained iron, aluminium, silicon, calcium, carbon dioxide, and traces of magnesium and manganese. A litre of water contained 0·8610 gram NaHCO₃, 0·1233 Ca(HCO₃)₂, 0·1113 Mg(HCO₃)₂, 0·0101 Fe(HCO₃)₂, 0·0660 CaSO₄, 0·1151 CaCl₂, 0·9057 MgCl₂, 0·0347 MgBr₂, 0·0316 MgI₂, 0·3647 KCl, 15·5999 NaCl, 0·1648 Al₂O₃, 0·0122 SiO₂, and small traces of manganese, ammonia, and phosphates. The residue obtained by evaporating a litre of water and heating at 180° weighed 18·2575 grams, but after heating to a red heat, only 17·5800. E. W. W.

Physiological Chemistry.

Fertilisation, Artificial Parthenogenesis, and Cytolysis in the Sea Urchin. JACQUES LOEB (*Pflüger's Archiv*, 1904, 103, 257—265. Compare Abstr., 1902, ii, 707).—A further contribution to a subject on which the author has already written much. The results form an extension of the views previously expressed. W. D. H.

Mechanism of Oxygen Supply to the Body. ADOLF LOEWY and NATHAN ZUNTZ (*Chem. Centr.*, 1904, i, 1452—1453; from *Arch. Anat. Physiol., physiol. Abth.*, 1904, 166—216).—The tension of dissocia-

tion of oxyhæmoglobin is dependent on the method adopted to prepare it; if alcohol is used, it is smaller than when the use of that reagent is avoided; laking the blood also lowers the tension. Figures are given to illustrate these facts. The resistance of the alveolar wall to gases was investigated in the frog's lung, the gas used being carbon dioxide. The influence of certain reagents on the process is given, and the results stated per square centimetre of lung surface; the entry of oxygen from the alveoli to the blood and from the blood to the tissues occurs easily at low pressures, and there is no need to postulate agencies at work other than physical.

W. D. H.

Action of Strychnine on the Respiratory Centre. H. BIBERFELD (*Pflüger's Archiv*, 1904, 103, 266—275).—After morphine has been administered and respiration thus slowed, intravenous injection of strychnine in rabbits produces an increase in rate and depth of respiration; the same (but more especially in the depth of respiration) occurs also when both vagus nerves are divided high in the neck. The effect of strychnine on the respiration of normal animals is very slight.

W. D. H.

Diurnal Variations in Blood Corpuscles. HERBERT C. WARD (*Amer. J. Physiol.*, 1904, 11, 394—403).—In the morning, the red corpuscles are relatively high in number; this declines in the afternoon, and rises again next morning. The hæmoglobin follows the same course. Meals and occupation seem to be the principal factors concerned. The leucocytes vary also, and approximately in the opposite direction; details concerning the different kinds of leucocytes are given.

W. D. H.

Proteolytic Ferment in Leucæmic Blood. FRANZ ERBEN (*Beitr. chem. Physiol. Path.*, 1904, 5, 461—462).—Schumm doubts whether the presence of a proteolytic ferment in leucæmic blood is the explanation of the occurrence of proteolytic products there. Since then the author has prepared from such blood, extracts which contain both a tryptic and a peptic enzyme; the latter is present in small amount only.

W. D. H.

Resistance of Proteid to Tryptic Digestion in the Animal Organism. SIEGFRIED ROSENBERG and CARL OPPENHEIMER (*Beitr. chem. Physiol. Path.*, 1904, 5, 412—421).—The resistance of unaltered horse serum to tryptic digestion has been previously described. The same holds true for other "genuine" proteids in experiments *in vitro*, and also *in vivo* if the material is injected into the intestine 30 centimetres below the pylorus in the dog, that is, below the situation of Brunner's glands. The absorption of fat is also small.

W. D. H.

Inhibition of Pepsin Activity by Salts. JULIUS SCHÜTZ (*Beitr. chem. Physiol. Path.*, 1904, 5, 406—411).—Anions act inhibitingly on pepsin within much wider limits than cations; this corresponds with Pauli's results on the precipitation of proteids by salts, but the analogy otherwise breaks down. Of the cations, sodium is the most

powerful in its inhibiting action; the action is wholly additive or nearly so. The influence of the electric charge on inhibition is small.

W. D. H.

Composition of Pancreatic Juice. LUCIAN A. E. DE ZILWA (*J. Physiol.*, 1904, 31, 230—233).—The alkalinity of secretin juice is usually greater than that of pilocarpine juice. Alkalinity diminishes as secretion progresses, but it can be maintained by injecting sodium carbonate into the blood. Pilocarpine juice contains about four times as much solid material as secretin juice. The solids diminish as secretion progresses. The variations in the solids are almost entirely due to variations in the amount of proteids. The mineral matter is fairly constant, about one-quarter of it consisting of chlorides. Of the proteids, nearly three-quarters are coagulated by a temperature under 55° ; most of the remainder came down under 75° . There is no appreciable difference between the freezing points of serum and pancreatic juice. There is a larger quantity of nucleoproteid in pilocarpine juice than in secretin juice, probably from a toxic effect of the alkaloid on the cell substance.

W. D. H.

Relation of Autolysis to Proteid Metabolism. H. GIDEON WELLS (*Amer. J. Physiol.*, 1904, 11, 352—354).—Autolysis, so far as nitrogenous substances are concerned, was investigated in the liver; addition of extracts of thyroid, kidney, and spleen do not influence it. There is no effect such as Cohnheim found in glycolysis in muscle with the addition of pancreatic extract.

W. D. H.

Autolysis of Tissues. JANET E. LANE-CLAYPON and SAMUEL B. SCHRYVER (*J. Physiol.*, 1904, 31, 169—187).—The experiments conducted on intestinal mucous membrane, liver, and kidney show that a great degradation of tissues occurs after death; the nitrogenous extractives increase in all cases, and in that of the liver amount to more than 50 per cent. of the total during the first 24 hours after incubation. Three stages are distinguished: (1) one of small change, (2) rapid degradation, and (3) gradual autolysis represented on the tracings by a straight line. This is not influenced by perfusion or ammonium oxalate, and is the same whether carried out in saline solution or distilled water. It is therefore regarded as a chemical function of cell-protoplasm. The second stage is quicker in a fasting than in a well-fed animal. The organs of the fasting animal appear to contain more enzyme (or zymogen) set free automatically and acting as a protection against starvation.

W. D. H.

Autolysis of Testis and Spleen. PHOEBUS A. LEVENE (*Amer. J. Physiol.*, 1904, 11, 437—447).—All the glands so far studied form, on prolonged self-digestion, similar end-products, but there is a marked difference in their proportions. In testis and spleen, autolysis occurs best in weakly acid solutions; acetic acid was employed. In the case of the testis, tyrosine, various amino-acids, pyrrolidine-2-carboxylic acid (in small amount), aspartic and glutamic acids, and purine bases were identified; pyrimidine and hexone bases could not be identified with

certainty. In the case of the spleen, only the amino-acids were studied. W. D. H.

Uptake of Water and Salt by the Epidermis and the Hygroscopic Characters of Certain Horny Structures. WILHELM FILEHNE and H. BIBERFELD (*Beitr. chem. Physiol. Path.*, 1904, 5, 449—460).—An investigation of the passage of lanolin mixed with water and salts into epidermal structures. Lanolin itself is not hygroscopic, and the uptake of water and salt by the human epidermis is very small and is not increased by the presence of lanolin. The amount absorbed varies in different individuals, and is with weak solutions relatively greater than with strong solutions of salt.

W. D. H.

Feeding with Cholic Acid in Cystinuria. CHARLES E. SIMON and D. G. CAMPBELL (*Beitr. chem. Physiol. Path.*, 1904, 5, 401—405).—The amount of neutral and oxidised sulphur in the urine varies considerably. On "normal" days, the neutral sulphur varies from 16 to 61 per cent. of the total, and averages 34 per cent. On days on which cholic acid was given, the average percentage was 24.8. It is regarded as doubtful if this really implies lessening of the cystin excreted. Various other possibilities are discussed.

W. D. H.

Utilisation of Vegetable Proteid by the Animal Organism. ELBERT W. ROCKWOOD (*Amer. J. Physiol.*, 1904, 11, 355—369).—Vegetable proteid, as judged by the nitrogen in the faeces, is less utilised than animal proteid. This is apparently due to admixture with other substances, for in experiments with the separated proteid from oats, no such disadvantage occurred. Cooking produced no marked difference. The experiments were made on dogs and men.

W. D. H.

Formation of Sugar from Proteid and Fat in the Animal Body. EDUARD PFLÜGER (*Pflüger's Archiv*, 1904, 103, 1—66).—Polemical against Luthje (*Münch. med. Woch.*, 1902, 1601). Doubt is cast on his results and conclusions, namely, whether the animals used were completely carbohydrate free, whether pancreatic extirpation really produces diabetes, and whether in the organism glycogen is formed from proteid and from fat.

W. D. H.

Formation and Elimination of Urea in Man. HENRI LABBÉ and MORCHOISNE (*Compt. rend.*, 1904, 138, 1636—1639).—The amount of urea excreted varies with the amount of nitrogen in the food, and is less when vegetable food is taken.

W. D. H.

Muscular Contraction and Energy. AUGUSTE CHAUVEAU (*Compt. rend.*, 1904, 138, 1465—1470).—By means of a new apparatus, the conditions of muscular work in man can be accurately gauged under varying conditions. During work, the amount of oxygen absorbed is roughly proportional to the work done; by working slowly, for instance, two contractions instead of thirteen per minute, the actual

values of the oxygen absorbed are reduced. The respiratory quotient always rises. Two kinds of contraction are studied, namely, *static*, in which the weight is not actually raised, but the muscles of the forearm work against a measured resistance, and *dynamic*, in which the weight is raised.

W. D. H.

Intraorganic Combustion. J. TISSOT (*Compt. rend.*, 1904, 138, 1545—1547).—From experiments on the dog, the following conclusions are drawn: a considerable diminution of oxygen-tension in the air produces a lessening of oxygen in the blood, even although an increase of pulmonary ventilation takes place. But this is not accompanied by any modification in the intensity of the respiratory exchanges. Intraorganic combustion is therefore independent of the amount of oxygen in the arterial blood.

W. D. H.

Action of Oxygen on Frog's Nerves. K. H. BAAS (*Pflüger's Archiv*, 1904, 103, 276—281).—Experiments are described which confirm Baeyer's results (*Zeit. allgemein. Physiol.*, 2, 169) that oxygen is necessary for the continued activity of excised frog's nerves. The normal nerve is considered to participate in respiratory metabolism.

W. D. H.

Glycogen in Organs. HERMANN LOESCHKE (*Pflüger's Archiv*, 1904, 102, 592—631).—The research shows that glycogen is not chemically bound in the liver and other tissues where it occurs, as Nerking considered. It is possible to extract it all by the prolonged use of hot water. What difficulty there is in extraction is also found in artificial mixtures of glycogen and albumin. By extraction with dilute alkali hydroxide, there is usually loss of glycogen if the process is prolonged; a part of the glycogen is converted into substances soluble in alcohol.

W. D. H.

Secretion of Acid by the Kidney. ARTHUR R. CUSHNY (*J. Physiol.*, 1904, 31, 188—203).—The acidity of urine in diuresis varies within strict limits. It is never alkaline to phenolphthalein nor acid to methyl-orange, and thus corresponds with the interval in reaction between mono- and di-sodium phosphate. The intravenous injection of most saline diuretics is followed by a marked fall in the percentage acidity, partly because the phosphates are deficient, and partly because absorption in the tubules is lessened. Phosphates injected in the same way increase urinary acidity, especially if the absorption in the tubules is increased. This is explained by the dissociation of the phosphates of the glomerular fluid, which permits of absorption of the cation along with hydroxyl or carbonate anions. These can permeate the epithelium, while the phosphate anion fails to do so freely, and so remains in the tubules along with the hydrogen cations replacing the original ones. The essential factors in the secretion of acid urine are (1) the presence of salts in the glomerular fluid which are capable of extensive hydrolysis, and of which the cations can permeate the epithelium, while the anion fails to do so equally readily; and (2) sufficient absorption in the renal tubules. Phosphates fulfil

these conditions. Carbonates fail to do so because the anion is absorbed, and the borates satisfy the conditions only in relation to phenolphthalein, because the anion is too weak to compete with the stronger anions of litmus.

W. D. H.

Urinary Chromogen due to Subcutaneous Injection of Scatole. CH. PORCHER and CH. HERVIEUX (*Compt. rend.*, 1904, 138, 1725—1727).—On a rigid milk diet, indole derivatives disappear from the urine. If scatole is then injected, a chromogen appears in the urine, which is not a derivative of indole, but no statement can as yet be made as to its composition.

W. D. H.

Sensibility to Carbon Dioxide diminished by Barometric Depression. ANGELO MOSSO (*Atti R. Accad. Lincei*, 1904, [v], 13, i, 591—597).—Experiments on rabbits and monkeys show that in a rarefied atmosphere containing a constant proportion of carbon dioxide, the exciting action of the latter is diminished, and, further, that by depressing the force of the respiratory movements below the normal value, the rarefaction causes a slight paralysis of the nervous centres regulating the respiration.

T. H. P.

Inhibitory Influence of Potassium on the Heart. E. G. MARTIN (*Amer. J. Physiol.*, 1904, 11, 370—393).—Inhibition produced by vagus stimulation and by potassium on the heart of the terrapin are very similar. The analogy does not hold in every detail, but explanations are given to account for the differences.

W. D. H.

Physiological Effects of Radium. C. J. SALOMONSEN and G. DREYER (*Compt. rend.*, 1904, 138, 1543—1545).—Exposure of animalcules to the radium emanations causes their death in time; amœbæ are more resistant than *Nassula*; before death, their movements become lessened, multiplication is inhibited, and cyst formation prevented. Trypanosomes are readily killed; mammalian blood is hæmolysed.

W. D. H.

Action of Adrenaline. T. R. ELLIOTT (*Proc. physiol. Soc.*, 1904, xx—xxi; *J. Physiol.*, 31).—Further experiments to show that the effect of adrenaline on plain muscle is the same as that produced by exciting sympathetic nerves. In an animal dying after excision of the suprarenals, the plain muscle has not only lost tone, but may even fail to respond to excitation of the sympathetic nerves, although sensory and motor nerves to voluntary muscle are still efficient. The sympathetic ganglia and the suprarenal medulla have a common embryological origin; perhaps the presence of adrenaline is necessary, and this substance may be secreted by sympathetic ganglia. But adrenaline does not excite the ganglia as nicotine does when applied to them locally; its effective action is localised at the periphery. Nevertheless, after complete denervation, the plain muscle of the dilator pupillæ responds to adrenaline, in fact more readily than in the intact iris. Adrenaline, therefore, cannot excite any structure derived from

or dependent for its persistence on the peripheral neuron. On the other hand, it evokes no reaction in muscle which has never been innervated by the sympathetic (Brodie and Dixon); the chemical excitant, adrenaline, which is liberated on each occasion when the impulse arrives at the periphery, must act on some mechanism developed out of the muscle-cell in response to its union with the synapsing sympathetic fibre, the function of which is to receive and transform the nervous impulse.

W. D. H.

Action of Eserine and Atropine on the Denervated Sphincter Iridis. HUGH K. ANDERSON (*Proc. physiol. Soc.*, 1904, xxii—xxiv; *J. Physiol.*, 31).—A certain time after the nerves of the iris have been cut, eserine causes once more a contraction of the sphincter. This is overcome by atropine. The reappearance of contraction disappears when the nerves are once more cut, and is therefore due not to independent excitability of the muscle itself, but to regeneration of nerve fibres, although other evidence of restoration of function (response to light or to direct stimulation of the nerves) is absent.

W. D. H.

Hay-fever. R. ASHLEIGH GLEGG (*J. Hygiene*, 1904, 4, 369—406).—The pollen which excites this disease owes its toxicity to an albuminous substance. As little as 0.000025 mg. will cause conjunctivitis in a person predisposed to the disease. The active proteid is an albumin: it is mixed with an inactive globulin. Injection of larger doses causes serious symptoms. An antitoxin has been prepared and gives excellent results.

W. D. H.

Application of the Laws of Chemical Equilibrium to Mixtures of Toxins and Antitoxins. WALTHER NERNST (*Zeit. Elektrochem.*, 1904, 10, 377—380).—The author criticises the conclusions of Arrhenius and Madsen (*Abstr.*, 1903, ii, 561). He points out that it is not proved that the reaction between toxins and antitoxins is reversible, and that the way in which Arrhenius and Madsen have applied the laws of chemical equilibrium is incorrect, as they have assumed two different equilibrium constants for the same reaction. He suggests that the smaller toxin molecule is perhaps absorbed by the larger colloidal antitoxin molecule, and that it subsequently undergoes a change of nature, much as a colouring matter is first absorbed by the fibre and then changed into an insoluble condition.

T. E.

Hepatotoxic Action of the Blood after Intraperitoneal Injection of the Nucleo-proteids of the Liver. H. BIERRY and ANDRÉ MAYER (*Compt. rend.*, 1904, 138, 1639—1640).—Hepatotoxins are developed, analogous to nephrotoxins, after injection of liver nucleo-proteid. The degenerative effects seen histologically in the liver are described.

W. D. H.

Toxicity of Selachian Blood. EUGÈNE GLEY (*Compt. rend.*, 1904, 138, 1547—1549).—Mosso showed that eel's blood is poisonous.

The present research shows that the serum of the torpedo ray is toxic to dogs, rabbits, and guinea-pigs. One to 2 c.c. per kilo. of body-weight kills a rabbit; with smaller doses, there is lowering of blood-pressure and of body-temperature, paresis, and other symptoms. The frog is more resistant. If the serum is heated to 57° , it loses its poisonous properties. The hæmolytic action of the serum is very marked; by gradually increasing doses, immunisation can be produced.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Action of Vanadic Acid on Micro-organisms. THOMAS BOKORNY (*Chem. Zeit.*, 1904, 28, 596—597).—The antiseptic action of vanadic acid on yeasts, moulds, and certain bacteria has been found to be very slight. A McK.

Decrease of Acid in Wine and the Process of Fermentation Involved. W. SEIFERT (*Bied. Centr.*, 1904, 33, 488—490; from *Zeit. Landw. Versuchswes. Oesterr.*, 6, 567—585).—The decrease of acidity in wine is caused by special bacteria, especially *Micrococcus malolacticus*. Malic acid is converted into lactic acid and a very small amount of volatile acids; other acids (succinic, *d* tartaric, *l*-tartaric, citric, malonic, lactic, and acetic acids) are not attacked. In alcoholic solutions, a production of acetic acid may take place. When malic acid and sugar are present, an increase in acidity takes place, more acid being produced than lost.

Yeast acts comparatively slightly on malic acid and does not produce lactic acid. Acetic acid bacteria may also decompose malic acid as well as many other acids.

The micrococcus decomposes malic acid in presence of 12—13 per cent. (vols.) alcohol, and its activity is increased by inactive or dying yeast. Its action is only slight in the case of wines deficient in nitrogen. N. H. J. M.

Production of Volatile Phosphorus Compounds in Putrefaction. CH. YOKOTE (*Arch. Hygiene*, 1904, 50, 118—127).—No volatile compound of phosphorus was obtained from putrefying brain, fish, or cheese during 10—20 days, and no reduction of sodium phosphate or sodium hypophosphite was observed. The experiments were under both aerobic and anaerobic conditions.

The conclusion is drawn that no reason exists for supposing that the gases produced during putrefaction readily become injurious owing to the presence of hydrogen phosphide.

Two sources of error were detected and avoided. When india-rubber is employed, positive results may be obtained; a second error may be caused by the compound of silicic acid with ammonium molybdate being supposed to be the phosphoric acid compound.

N. H. J. M.

Decomposition of Selenium Salts by means of Micro-organisms. B. GOSIO (*Atti R. Accad. Lincei*, 1904, [v], 13, i, 642—645).—Like the tellurites (see this vol., ii, 503), the selenites are readily attacked by micro-organisms, with formation of a red substance, probably metallic selenium. This decomposition is brought about by a very large number of micro-organisms and may be used for the detection of bacterial life. The most suitable method of carrying out the reaction is to add 1 or 2 drops of a 20 per cent. solution of the selenite to a vigorous culture, best 20—24 hours old, of the organism. At a favourable temperature, the change becomes visible in about 10 minutes and a copious precipitate forms in 30—40 minutes. The sensitiveness of the selenite to change by any particular organism is best observed by mixing the selenite with the culture medium before inoculation. The author divides bacteria into 3 groups, the members of which give with a selenite (1) a very marked reaction, (2) a less marked but distinct reaction, and (3) a doubtful reaction. T. H. P.

Formation of Hydrogen Sulphide by Alcoholic Fermentation. M. EMMANUEL POZZI-ESCOT (*Chem. Centr.*, 1904, i, 1661; from *Bull. Assoc. Chim. Sucr. Dist.*, 21, 1071—1073).—When a sulphate or sulphite is contained in a liquid which is undergoing alcoholic fermentation, hydrogen sulphide is formed and the wines acquire a characteristic putrid taste. Hydrogen sulphide is also frequently generated in the manufacture of spirits, especially from molasses. The formation of this gas is always associated with a disturbance of the normal functions of the yeast. The source of the yeast, its method of culture, the filling of the vat, and the kind of fermentation are factors which may influence the result. E. W. W.

Action of Alkaline Salts on Living Substance. N. C. PAULESCO (*Compt. rend.*, 1904, 138, 1728—1730).—The minimal amounts of various salts of the alkali metals which prevent the formation of carbon dioxide by yeast are given in tabular form. The amounts are proportional to their molecular weights. W. D. H.

Yeast from the Cane Sugar of Nicaragua. M. EMMANUEL POZZI-ESCOT (*Chem. Centr.*, 1904, i, 1661; from *Bull. Assoc. Chim. Sucr. Dist.*, 21, 1007—1008).—A sample of yeast from a distillery in Nicaragua has been found to contain yeast cells of a peculiar form which had a certain analogy to that of *Saccharomyces pastorianus*. The yeast and the fermented liquor had the odour of the cane sugar juice. At the ordinary temperature, dextrose and maltose are only partially fermented by the yeast, but at 30—35° the action is rapid, maltose being the more quickly attacked; lactose and galactose are completely oxidised. Wines containing 14—15 per cent. of alcohol may be obtained by means of this yeast, even when used before it is completely acclimatised. Under suitable conditions of temperature, the yeast does not appear to be injured by the presence of a large quantity of sugar. E. W. W.

Length of Life of Dried Yeasts. H. WILL (*Chem. Centr.*, 1904, i, 1578—1579; from *Zeit. f. ges. Brauw.*, 27, 269—271).—The examination of a number of old samples of dried yeasts has shown that yeast, generally speaking, retains its vitality for an extremely long time. Not only do the various groups of yeasts differ, however, in this respect, but the members of these groups are also unlike. The wild yeasts were found to live longer than the cultivated yeasts, even in cultures which consisted mainly of beer yeasts. In a sample preserved with asbestos, a wild yeast was found to be alive after $17\frac{1}{4}$ years. *Saccharomycetes apiculatus*, preserved with wood, had retained its vitality after 3 years, but not after $10\frac{1}{4}$. The top-fermenting succumbed in less time than the bottom-fermenting yeasts, and in no case lived more than $10\frac{1}{4}$ years. A large number of cells of a bottom-fermenting yeast mixed with wood-charcoal were found to be capable of causing fermentation after 13 years and 2 months. The length of life is also dependent on other conditions, and especially on the nature of the material with which the yeast is mixed. Wood charcoal appears to be the most favourable for the retention of vitality, and gypsum and kieselguhr less so than wood or asbestos. Temperatures below 0° prolong life, whilst higher temperatures shorten it. Exclusion of air and a comparatively low amount of water which is not subject to alteration by variation of other external conditions also act favourably. From 3—6 per cent. of water appears to be the most suitable amount. The method used in drying the yeasts has also some influence on the duration of life.

E. W. W.

Detection of Beer Yeast in Press Yeast by means of Biological Analysis and the Introduction of a Definite Type of Yeast in the Manufacture of Press Yeast. PAUL LINDNER (*Chem. Centr.*, 1904, i, 1579; from *Zeit. f. ges. Brauw.*, 27, 269—271).—This paper refers mainly to matters of biological rather than of chemical interest. The different types of yeast may be distinguished by their initial forms of germination. The homogeneity of a yeast may be tested by comparing the germination forms in a number of drop cultures.

At least 90 per cent. of the commercial press yeasts form branched germination forms, and the cells do not appear to adhere together and form flakes in the way most bottom-fermenting yeasts do.

E. W. W.

Mode of Utilisation of Ternary Carbon by Plants and Microbes. PIERRE MAZÉ (*Ann. Inst. Pasteur*, 1904, 18, 277—303. Compare Abstr., 1902, ii, 577, 578, and 1903, ii, 36).—Yeast possesses a very limited anaërobic life. Under these conditions, acetic acid is produced at the expense of sugar, the yeast, at the same time, assimilating alcohol. The fermentation is thus similar to those produced by strictly anaërobic ferments, from which it, however, differs in not being able to obtain oxygen from water.

N. H. J. M.

Circulation of Odoriferous Compounds in Plants. EUGÈNE CHARABOT and G. LALOUÉ (*Compt. rend.*, 1904, 138, 1229—1231).—In young leaves, the essence is less rich in ethers and total alcohol

than the young stems. At the end of the vegetative period, the difference as regards ethers is much greater; the proportion of geraniol is less, and that of linalool greater, in the essence of the leaves than in that of the stems. The conclusion is drawn that the essence of orange stems is less soluble than that of the leaves.

The production of essential oils takes place in the green parts of plants, especially the leaves. A portion of the odoriferous compounds migrates from the leaves to the stems, where their solubility is diminished.

N. H. J. M.

Constituents of Asparagus. ERNST WINTERSTEIN and P. HUBER (*Zeit. Nahr. Genussm.*, 1904, 7, 721—730).—The percentage composition of the sap was as follows:

| Total. | Nitrogen | | | | | Carbo- hydrates. | Organic matter. | Ash. |
|--------|-----------------------|---------------------------------|--------------|----------------|------------------------|---------------------|--------------------|-------|
| | as total proteids. | as coagu- lable proteids. | as bases. | as ammonia. | as aspara- gine. | | | |
| 0.1695 | 0.0247 | 0.0174 | 0.0223 | 0.0092 | 0.0102 | 0.874 | 2.878 | 0.042 |

The dry matter contained: total nitrogen, 3.84; crude fibre, 16.41; furfuroids, 6.99; fat, 4.06; and ash, 9.16 per cent.

N. H. J. M.

Nuclein Bases in Juice of Beta Vulgaris. HARRY W. BRESLER (*Zeit. physiol. Chem.*, 1904, 41, 535—541).—The amount of nitrogen in the juice of *Beta vulgaris* is 0.2345 gram per litre. Of this nitrogen, 0.29 per cent. exists in the form of hetero-xanthine, 1.58 as guanine, 0.81 as xanthine, 0.61 as adenine, 0.91 as hypoxanthine, and 0.69 per cent. as carnine. Full details for the separation of the different compounds are given.

J. J. S.

Composition of Carobs of Different Origins. BALLAND (*J. Pharm. Chim.*, 1904, [vi], 19, 569—571).—Specimens of commercial carobs are found to possess the following percentage compositions: water, 9 to 13; nitrogenous compounds, 5 to 7; cellulose, 8 to 12; fat, less than 1; ash, 2; sugars (dextrose and sucrose in variable proportions), 30 to 43; phosphoric oxide, 0.16 to 0.24.

G. D. L.

Various Kinds of Cinnamon. JOSEF HANUŠ (*Zeit. Nahr. Genussm.*, 1904, 7, 669—672).—The following amounts of cinnamaldehyde were found in different varieties of cinnamon, the method employed for the estimation being that previously described by the author (*Abstr.*, 1903, ii, 768): Ceylon cinnamon, 1.74—2.19 per cent.; cassia cinnamon, 2.08—3.81 per cent.; the buds of the latter, 3.70—6.00 per cent.; and cinnamon chips, 1.23—1.42 per cent. Other barks containing cinnamaldehyde and some so-called cinnamons were also examined, the results obtained being: East Indian cinnamon (*Cinamomum Tamata*), 1.80 per cent.; wild Ceylon cinnamon, branches, 0.12; stem, 1.80 per cent.; Massoy cinnamon from Java (*C. Kiamis Nees*), none; *C. ceylanici* Nees, a trace; clove cinnamon (*Cassia caryophyllata*), 1.51 per cent.; and "white" cinnamon (*Canella alba*), none.

The whole of the cinnamaldehyde was found to be removed from cinnamon by distilling in a current of steam. It was also ascertained that no aldehyde was present in the form of glucosides. W. P. S.

The Gum of *Mangifera indica*. P. LEMELAND (*J. Pharm. Chim.*, 1904, [vi], 19, 584—593).—The gum contains 16.57 per cent. of moisture and 3.357 per cent. of ash, and the dry substance is soluble in water to the extent of 39.36 per cent., the solution having $[\alpha]_D - 25.33^\circ$. The gum contains an oxydase, yielding a red colour with guaiacol solution.

It contains 71.42 per cent. of sugars, including 25.33 of galactose, and 35.095 of pentoses (arabinose was also separated).

The portion insoluble in water contains moisture, 10.51; and in the dry substance, galactose, 32.08; pentoses, 42.87; total glucoses, 86.28 per cent., having $\alpha_D + 64.89^\circ$. G. D. L.

Presence of Quinol in the Pear Tree. G. RIVIÈRE and G. BAILHACHE (*Compt. rend.*, 1904, 139, 81—83).—Quinol to the extent of 3—5 grams per kilogram can be extracted by ether from the buds of the pear tree (*Pyrus communis*), the maximum yield corresponding with the most active stage of vegetation; it is not found in the mature plant because it is oxidised to quinone by the laccase, identical with that of Bertrand (compare this vol., i, 157), contained in the plant. The buds of the apple tree contain phloridzin, but not quinol.

M. A. W.

Fatty Oil of Strawberries. I. APARIN (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 581—596).—The oil obtained from strawberries has a sp. gr. 0.9345 at $15^\circ/4^\circ$ and $n_D 1.4790$ at 25° ; saponification number, 193.7; acid number, 6.41; Reichert-Meissl number, 2.1; Hubl's iodine number, 180.3. The insoluble fatty acids of the oil amount to 88.2 per cent., their iodine number being 192.3. The principal acids present are: linoleic acid, about 81 per cent.; linolenic acid, about 10.5 per cent.; and oleic acid. T. H. P.

Relation of Mass Action and Physical Affinity to Toxicity. J. B. DANDENO (*Amer. J. Sci.*, 1904, [iv], 17, 437—458).—Numerous experiments have been made by various observers on the toxic effect of different chemical compounds on seedlings (see this vol., ii, 283). The author considers that in many of these the death of the seedling was uncertain, and that all failed to take into account a most important factor, namely, the quantity of the solution employed, as his own experiments prove this to be of the utmost importance. The evidence of death of the seedling adopted was inability to afterwards grow in water. The effect of quantity of solution is seen by the fact that in hydrochloric acid of strength $N/2048$ seedlings would live if the quantity of acid was not greater than about $2\frac{1}{2}$ c.c., but died if it exceeded this amount. Similar results were obtained for all the compounds and seedlings, the concentration causing death depending upon the quantity employed. It was also found that the toxic effect was very materially lowered by the addition of substances chemically

inactive, as, for example, sand. The toxic effect of carbonic acid is very low, and the author considers it probable that hydrolytic dissociation of carbonates takes place. He protests very strongly against the attempts to always make the physiological effects fit in with the dissociation theory by ascribing all discrepancies to the effect of the undissociated molecule.

L. M. J.

Catalytic Properties of Grain and Meal. NEUMANN WENDER and D. LEWIN (*Chem. Centr.*, 1904, i, 1530; from *Oesterr. Chem. Zeit.*, 7, 173—175).—By determining the quantity of oxygen which is liberated from hydrogen peroxide, it has been shown that the enzymes which have a catalytic action do not increase during the germination of the grain. By suitably varying the conditions of temperature, the diastatic properties of the enzymes may be destroyed without affecting their catalytic power. Ether or a solution of 96 per cent. of alcohol by volume has no injurious effect on the enzymes, but a 0.1 per cent. solution of mercuric chloride or silver nitrate, a 0.2 per cent. solution of potassium hydroxide, or a 1 per cent. solution of acetic acid or of hydrochloric acid destroys them. Hydrogen peroxide is rapidly attacked by the meal or the macerated grains. Bran has a very much greater catalytic action than meal of the same kind of corn. The meal prepared from the exterior portions of the grains contains considerably more catalase than that from the interior. Since the catalytic power of a meal is less the finer its state of division, it is possible to distinguish the different kinds of meal by a simple method based on this fact.

E. W. W.

Quantity of Soluble and Coagulable Nitrogen contained in Malt. KARL DINKLAGE (*Chem. Centr.*, 1904, i, 1529; from *Zeit. ges. Brauw.*, 27, 249—251. Compare *ibid.*, 26, 585).—The total nitrogen, the soluble nitrogen, and the coagulable portion of the latter have been determined in the case of 8 bright golden malts of the Pilsener and Vienna types and 13 dark malts of the Munich character. The colour of the former varied from 0.15 to 0.3 and of the latter from 0.55 to 2.35 *N*/10 iodine solution. The malts contained from 1.5 to 1.8 per cent. of nitrogen (9.4—11.4 per cent. of proteid) calculated on the dry malt, with the exception of one sample which gave a lower value and two which contained more. The results show that, generally speaking, the amounts of soluble and coagulable nitrogen are independent of the total nitrogen or proteid contained in the malt, but that some relationship exists between the soluble and the coagulable nitrogen. When the temperature of the kiln is raised, both the quantity of soluble nitrogenous material and the coagulable portion decrease, the effect on the latter being greater than on the former. From the results obtained, it may be concluded that in cases of malts containing 9—11 per cent. of proteid, the bright golden-yellow malts contain 0.48—0.54 of soluble and 0.11—0.13 per cent. of coagulable nitrogen, whilst the dark and very dark malts contain 0.39—0.48 per cent. of soluble nitrogen. The coagulable nitrogen of the dark malts varies from 0.08—0.11, and that of the very dark malts from 0.07 to 0.08 per cent. Malts which do not show relationships of this character

have an abnormal composition or have been subjected to unsuitable conditions in the kiln. E. W. W.

Amount of Tannin contained in Barley, Malt, and Worts to which Hops have not been added. ALBERT REICHARD (*Chem. Centr.*, 1904, i, 1449; from *Zeit. ges. Brauw.*, 27, 229—235, 253—258, 271—275).—The tannin compound contained in barley is soluble in alcohol or hot water, but the greater portion separates from the aqueous solution on cooling. The alcohol which is formed on germination subsequently dissolves a portion of the tannin compound, and the wort also contains this substance partly in a state of emulsion and partly as a finely divided powder or a coarse granular or flocculent precipitate. The latter forms cause turbidity in the beer, whilst the emulsion and fine powder form sediment of a particularly solid character ("beer stone"). The yeast cells themselves may also be injured by the sediment. A precipitate similar to that caused by the tannin compound is also formed by lactic acid in worts which do not contain hops, but the compound in this case is insoluble in alcohol.

E. W. W.

Migration of Odoriferous and Colouring Substances to Milk. S. DOMBROWSKI (*Arch. Hygiene*, 1904, 50, 183—191).—The milk of goats fed with *semina anisi* and *fœniculi* acquired the odour of these substances. Similar results were obtained with garlic, the taste of which was retained by the milk even after boiling. In the case of fenchel and anis, the odour was moderately strong and disappeared when the milk was boiled. Feeding with yellow turnips and *Ac. chrysophanicum med.* imparted a very slight amount of colour to the milk.

When milk was kept for half an hour in a room with iodoform and *oleum anisi*, the odour of these substances was rapidly acquired by the milk and was retained for twelve hours. The odours of phenol, *oleum terebinthini*, and formalin are also rapidly acquired, but are soon lost. The odour of bleaching powder was only to a slight extent imparted to the milk.

N. H. J. M.

Constituents of Emmenthaler Cheese. II. ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1904, 41, 485—504. Compare Abstr., 1902, ii, 687).—The following nitrogenous compounds have been isolated from a three-months-old Emmenthaler cheese and are regarded as primary decomposition products: glycine, alanine, aminovaleric acid, leucine, pyrrolidine-2-carboxylic acid, aspartic acid, glutamic acid, tryptophan, histidine, and lysine. The amounts of these products vary in different cheeses. Simpler nitrogenous compounds, namely, ammonia, guanidine, tetramethylenediamine, and pentamethylenediamine, also occur and are regarded as secondary decomposition products, probably derived from arginine and lysine.

The presence of hydroxy-amino-acids has not been definitely settled. Succinic, lactic, and citric acids are always present together with peptones (polypeptides?).

Choline was extracted from a ripe cheese which produced poisonous effects.

Caseoglutin (Abstr., 1902, ii, 688), on hydrolysis with concentrated hydrochloric acid, yields histidine, 2.3; arginine, 1.26; and lysine, 2.9 per cent. J. J. S.

Removal of Poison from Tobacco Smoke. HERMANN THOMS (*Bied. Centr.*, 1904, 33, 482—483; from *Chem. Zeit.*, 1904, 28, 1).—The essential constituents of tobacco smoke are nicotine, pyridine bases, ammonia, methylamine, pyrrole, hydrogen sulphide, hydrogen cyanide, butyric acid, carbon dioxide and monoxide, phenol, and tarry products. It was found that cotton wool soaked in a solution of ferric chloride in glycerol retains the very poisonous ethereal oil, the hydrogen sulphide, and about half of the hydrogen cyanide and nicotine. A complete absorption of the products is not possible, besides being, of course, undesirable.

RICHARD KISSLING (*ibid.*, 483—484) points out that the extent of absorption depends on the time employed, and that in practice the speed of the smoke would be about eight times that attained in the experiments. N. H. J. M.

Occurrence of Unusually Large Amounts of Injurious Sulphur Compounds in Peat. HERMANN MINNSEN (*Bied. Centr.*, 1904, 33, 433; from *Mitt. Ver. Förd. Moorkultur*, 1904, 1).—A sample of surface soil (peat) from Siberia contained 3.940 per cent. of sulphuric acid as ferrous sulphate and 3.346 per cent. of free sulphuric acid, besides 25.595 per cent. of undecomposed iron sulphide. The subsoil (20—60 cm.) contained 7.059 per cent. of sulphuric acid as ferrous sulphate, 6.055 per cent. of free acid, and 37.15 per cent. of iron sulphide. The total sulphur (as SO_3) in forms injurious to vegetation amounts to 203,458 kilos. per hectare in the surface soil (to 20 cm.) and 108,400 kilos. in the subsoil.

The original surface of the soil, to a depth of over 2 feet, had been removed a long time before the samples were taken. N. H. J. M.

Ammonia or Sodium Nitrate? H. CLAUSEN (*Bied. Centr.*, 1904, 33, 434—437; from *Ill. landw. Zeit.*, 1903, 892).—In 1901, with high rainfall in April and May, ammonium salts gave very good results, the yields of winter rye and potatoes being considerably greater than with sodium nitrate. In 1902, with a dry April and a wet May, sodium nitrate gave the best results with rye, whilst in the case of oats the best results were obtained with ammonium salts.

N. H. J. M.

Manurial Experiments with Lime. DMITRI PRIANISCHNIKOFF (*Jour. exper. Landw.*, 1903, 4, 267—268).—The results of experiments with wheat and lupins grown in Russian black soil without lime and with 0.25, 0.5, and 1 per cent. of lime showed that the yields of both increased with the amount of lime. The yield of oats, in acid loam soil, was greatly increased by 0.5 per cent. of lime, and was reduced by 1 per cent.

The general opinion that lime is injurious to lupins is probably due to their usually being grown in sandy soils.

Small amounts of lime were distinctly beneficial to nitrification in black soil.

N. H. J. M.

Analytical Chemistry.

Use of Hydrogen Chloride in Volumetric Analysis. GEORG LUNGE (*Zeit. angew. Chem.*, 1904, 17, 886).—The author observes that the process proposed by Raschig (this vol., ii, 441) has already been described by Moody (*Trans.*, 1898, 73, 658). L. DE K.

Estimation of Sodium Perchlorate in Saltpetre. H. LEMAÎTRE (*Chem. Centr.*, 1904, i, 1427—1428; from *Mon. Sci.*, [iv], 18, 253—254).—Five grams of the dried sample are mixed with 3 grams of dried sodium sulphite and fused in a platinum crucible. The mass is dissolved in water and mixed with 200 c.c. of a 4 per cent. barium nitrate solution. The filtrate is boiled with 8.2 c.c. of *N*-alkali hydroxide and 1.2 gram of sodium persulphate, and, after filtering, the liquid is first neutralised with acetic acid, using phenolphthalein as indicator, and the chlorine is then titrated with *N*/10 silver solution. Any iodine present may be estimated colorimetrically by Anzenat's method. L. DE K.

Estimation of Sulphuric Acid in the Presence of Iron. GEORG LUNGE (*Zeit. angew. Chem.*, 1904, 17, 913—917, 949—953).—Silberberger (*Abstr.*, 1903, ii, 751) has proposed to substitute strontium chloride in alcoholic solution for barium chloride, and has even recommended the process for the estimation of sulphur in pyrites, stating that Lunge's barium chloride process, which involves the previous separation of the iron with ammonia, cannot be said to be accurate as there is a loss caused by the retention of sulphuric acid in the iron precipitate, which is, however, more or less compensated by the impurities in the barium sulphate.

The author defends his process against Silberberger's attack and also criticises the strontium process, which, although accurate enough for sulphates, cannot be used in the presence of iron, as the strontium sulphate is strongly contaminated with iron, which causes the result to be untrustworthy. A further drawback to the strontium process is the difficulty in obtaining clear filtrates. L. DE K.

Estimation of Nitrogen according to Dumas' Method. ANTON LANDSIEDL (*Chem. Zeit.*, 1904, 28, 643—644).—A convenient form of measuring tube is described for collecting the nitrogen during a Dumas estimation. A. McK.

Estimation of Phosphorus and Nitrogen in Organic Substances. FRITZ VON KONEK (*Zeit. angew. Chem.*, 1904, 17, 886—888).—About 0.5 gram of the substance reduced to an impalpable powder is mixed by means of a wire with 10—15 grams of sodium peroxide contained in a nickel crucible. If the substance is very poor in carbon, a little of some highly carbonaceous material should be added. After screwing on the lid, the crucible is placed in cold water and the contents are fired by a red-hot wire. The mass now contains the phosphorus as phosphate and the nitrogen as nitrate, which are then estimated by the usual processes. L. DE K.

Estimation of Arsenic. JOHN KÖHLER (*Arkiv Kem. Min. Geol.*, 1904, 167—184. Compare Klason and Köhler, *Abstr.*, this vol., ii, 208).—In the ordinary methods for estimating arsenic in wall-papers, &c., organic matter often distills over and interferes with the titration. The authors therefore recommend that the distillate be caught in nitric acid, evaporated, and treated with potassium permanganate and sulphuric acid until all the organic matter is destroyed. The arsenic compounds are then reduced to arsenious anhydride by means of sulphur dioxide in presence of a little sulphuric acid, and, after evaporating to remove excess of sulphur dioxide, the sulphuric acid is neutralised by means of sodium hydrogen carbonate. Instead of collecting the distillate in nitric acid, this may be replaced by potassium permanganate solution or a dilute solution of hydrogen peroxide, but subsequently excess of the latter must be removed completely. This method of procedure is found to yield good results.

On preparing mirrors of known amounts of arsenic by reduction with sodium carbonate and potassium cyanide, it was found that, using 1.0—0.1 mg. of arsenic, never more than 40 per cent. found its way into the mirror; the amount of the loss depends on the quantity of arsenic employed, the reduction method used, and the nature of the arsenic compound. Better results are obtained with the Marsh apparatus, but comparison of the arsenic mirror with standard mirrors is not good, and it is best to dissolve the mirror and determine the arsenic as above.

T. H. P.

Sodium Peroxide in Qualitative Organic Analysis. FRITZ VON KONEK (*Zeit. angew. Chem.*, 1904, 17, 771—774).—Into a strong cylindrical nickel or steel crucible, fitted with a perforated lid through which passes a 10 cm. long nickel or steel tube, are introduced 5—10 grams of pure sodium peroxide, and a pinch of the finely-powdered sample is added and thoroughly mixed by means of an iron wire. When dealing with volatile compounds, which must be tested for nitrogen, &c., a little of a compound rich in carbon, such as camphor, should be added. After fixing on the lid, the crucible is placed in a basin containing cold water, and the mass is then ignited by dropping a red-hot iron wire into the tube. The reaction is somewhat violent, but free from danger; the experiment is therefore suitable for the lecture table.

The mass contains the carbon as carbonate, the nitrogen as nitrate, sulphur as sulphate, phosphorus as phosphate; halogens will be found

as oxygen compounds. The usual tests for these various substances are then applied. As regards the nitrogen, the author thinks his process is an improvement on Lassaigne's test, heating with metallic sodium and testing the mass for cyanide.

L. DE K.

Estimation of Organic Carbon by means of Sodium Peroxide. FRITZ VON KONEK (*Zeit. angew. Chem.*, 1904, 17, 888—891).—The method is briefly as follows: the substance (see preceding abstract) is oxidised with sodium peroxide, the mass is dissolved in water and made up to a definite volume. An aliquot part is then mixed with a solution of barium chloride of known strength until the carbonate is completely precipitated. The liquid is again made up to a definite bulk, and when the precipitate has completely settled it is passed through a rapid filter, and in an aliquot part of the filtrate the excess of barium is estimated by precipitation as sulphate. From this is calculated the amount of barium carbonate which has precipitated, and, of course, represents the organic carbon.

Great care should be taken to avoid as much as possible contact with the air, and the water used should be free from carbon dioxide. A blank experiment should also be made to ascertain the amount of carbon dioxide contained in the sodium peroxide. Sulphur, if present, should be estimated separately and allowed for.

L. DE K.

Spectrophotometric Estimation of Small Quantities of Carbon Monoxide in the Air. LOUIS DE SAINT-MARTIN (*Compt. rend.*, 1904, 139, 46—49).—When a dilute solution of fresh dog's blood containing about 0.15 per cent. of oxyhæmoglobin is shaken with 10 times its volume of air containing 0.20 to 1 per 1000 of carbon monoxide, the solution absorbs a small quantity of the gas forming carboxyhæmoglobin, and the ratio of the carboxyhæmoglobin to the original oxyhæmoglobin increases with the proportion of carbon monoxide in the air; the value of this ratio is determined by means of a spectrophotometric method for specimens of air containing 0.25, 0.50, 0.70, or 1.00 per 1000 of carbon monoxide, and a curve constructed having the ratios as ordinates and the proportions of carbon monoxide as abscissæ. By means of this curve, it is possible to determine the amount of carbon monoxide contained between the above limits in a sample of vitiated air; the air is agitated with the requisite quantity of blood solution, the value of y determined spectrophotometrically, and the corresponding value of x read from the curve.

M. A. W.

Estimation of Potassium. D. SIDERSKY (*Ann. Chim. anal.*, 1904, 9, 207—209).—An official report. For technical purposes, the potassium should be estimated by means of platinic chloride according to Fresenius' method. One gram of the platinum double salt represents 0.3056 gram of potassium chloride.

The estimation as potassium perchlorate, according to Schlöesing's method, also gives trustworthy results. One gram of perchlorate represents 0.5382 gram of potassium chloride.

L. DE K.

Estimation of Potassium. NAZARENO TARUGI (*Gazzetta*, 1904, 34, i, 324—341).—The principle of this method is as follows: when a suitably concentrated solution of sodium persulphate is added to a solution of potassium sulphate, the potassium persulphate formed mostly separates in a solid, crystalline condition, only a small proportion of it remaining in solution. By titrating the sodium persulphate solution with standard sodium hydroxide solution, both by itself and after mixing with the potassium salt and making a suitable correction for the potassium persulphate remaining in the solution, the amount of potassium salt in the original liquid can be determined.

The author has measured the solubility of potassium persulphate in water and in various salt solutions, which all give the same values, so that the allowance for solubility becomes greatly simplified. The solubility curve consists of four straight lines represented by the four equations: $y = 0.108x + 1.62$ (0° to 9°); $y = 0.008x + 2.52$ (9° to 10°); $y = 0.108x + 1.52$ (10° to 15°), and $y = 0.270x - 0.91$ (15° to 40°), where y is the solubility and x the temperature in $^\circ\text{C}$. From these values, the equations by which the corrections to be applied to the amount of K_2O found by this method are readily found, and are: $y = 0.0376x + 0.564$ (0° to 9°); $y = 0.00278x + 0.8773$ (9° to 10°); $y = 0.0376x + 0.529$ (10° to 15°), and $y = 0.094x - 0.3164$ (15° to 40°).

The concentration of the sodium persulphate solution should not be less than 14 per cent., and it is best to take 200 grams of the commercial salt and make up to 1 litre, afterwards filtering from any slight turbidity. To titrate this solution, 10 c.c. of it are diluted with distilled water to 100 c.c. and 5 c.c. of the diluted solution boiled for about 20 minutes, the evaporated water being replaced from time to time. A few drops of phenolphthalein are added, and $N/10$ sodium hydroxide solution run in until the red colour persists after 5 minutes' boiling. The sodium persulphate solution, which should be re-tested from time to time, should not deposit crystalline matter, even on the addition of a crystal of potassium persulphate.

In estimating the potassium in any product, a weighed quantity of about 1 gram of it is treated with concentrated sulphuric acid and afterwards heated and even ignited to expel the excess of acid and any ammonium salts. The residue is dissolved in 10 c.c. of water and the solution, filtered if necessary, mixed with 10 c.c. of the standard sodium persulphate solution and placed in a thermostat until its temperature becomes constant. A very small crystal of potassium persulphate is then added to precipitate that in solution. Ten c.c. of the clear, supernatant liquid are then removed, diluted to 50 c.c., and 5 c.c. of this solution titrated with $N/10$ sodium hydroxide solution as described above. The difference in the titre of the sodium persulphate solution before and after mixing with the potassium solution, allowing for the dilution, is multiplied by 0.0047, and the value thus obtained, corrected for the potassium persulphate dissolved, represents the K_2O present.

If no deposit of crystalline potassium persulphate can be obtained, even at 0° , a larger quantity of the material must be employed.

T. H. P.

Separation of Calcium and Magnesium. CARL STOLBERG (*Zeit. angew. Chem.*, 1904, 17, 741—744, 769—771).—A criticism of the oxalate process. When the magnesium strongly predominates, it has been recommended to effect a separation with sulphuric acid in the presence of alcohol; but, according to the author's experiments, it is difficult so to regulate the proportion of alcohol that the calcium is completely precipitated as sulphate without occlusion of magnesium sulphate. The following modification, however, yields good results.

The mixed calcium and magnesium salts are converted into anhydrous sulphates by heating with sulphuric acid until the excess of acid has completely evaporated. The dry mass is now treated with sufficient hot water to dissolve all the magnesium sulphate and then mixed with excess of a mixture of 10 vols. of absolute alcohol and 90 vols. of methyl alcohol. This causes the complete separation of the calcium sulphate without co-precipitation of magnesium, and after washing with a mixture of 5 vols. of absolute alcohol and 95 vols. of methyl alcohol, the precipitate is dried and ignited. L. DE K.

Volumetric Method for the Estimation of Mercury Fulminate. HENRY W. BROWNSDON (*Chem. News*, 1904, 89, 303—304).—For the estimation of mercury fulminate in cap or detonator compositions, the following method is given. From 0.12 to 0.25 gram of the composition is weighed into a 100 c.c. flask containing about 50 c.c. of water, 1 gram of pure sodium thiosulphate is added, and the contents of the flask well shaken until the fulminate is decomposed. This takes about 2 minutes. The mixture is then diluted with water to 100 c.c., filtered, and 25 c.c. of the filtrate titrated with *N*/10 sulphuric acid, using methyl-orange as indicator. The sulphuric acid is standardised on pure mercury fulminate prepared by dissolving the ordinary commercial product (1 mol.) in pure potassium cyanide (1 mol.) solution, precipitating the mercury fulminate from the solution of the double salt by means of dilute nitric acid, washing the precipitate with water until free from acid, and drying it at a temperature of 80—90°. The amount of mercury fulminate in the portion of composition taken for analysis should not exceed 0.05 gram, otherwise the alkali set free tends to react with the finely-divided antimony sulphide. W. P. S.

Standardisation of Permanganate Solutions. FREDERICK DUPRÉ (*Zeit. angew. Chem.*, 1904, 17, 815—817).—Treadwell has proposed to standardise permanganate solutions by means of electrolytically-precipitated metallic iron, and the author confirms the accuracy of the process. Equally trustworthy results may, however, be obtained by Volhard's iodometric process, in which the iodine liberated by permanganate from potassium iodide in acid solution is titrated with sodium thiosulphate. L. DE K.

Stability of Standard Solutions of Potassium Permanganate and Ammonium Oxalate. WALTER M. GARDNER and BARKER NORTH (*J. Soc. Chem. Ind.*, 1904, 23, 599).—The authors' experiments prove

that, both in the solid state and in solution, pure potassium permanganate remains unaltered in strength for at least 12 months, even when exposed to light, if kept in well-stoppered bottles. Solutions of ammonium oxalate were found to deteriorate at the rate of about 1 per cent. per fortnight. In the solid state, ammonium oxalate and ferrous ammonium sulphate retain their strength for at least 12 months.

W. P. S.

Iodometric Estimation of Ferric Iron. AUGUSTE HOLLARD (*Ann. Chim. anal.*, 1904, 9, 220).—The author states that he has used long ago the same process recently proposed by Namias and Carcano (this vol., ii, 368), substituting, however, carbon disulphide for chloroform.

L. DE K.

Analysis of Ferro-silicon. H. CANTONI (*Ann. Chim. anal.*, 1904, 9, 203—204).—0.5 to 0.6 gram of the finely-powdered substance is heated in a copper crucible with 7—8 grams of sodium peroxide. The fused mass is then removed from the crucible with warm water, and evaporated with excess of hydrochloric acid to separate the silica. The filtrate is freed from any copper by means of hydrogen sulphide, and the iron and other impurities are then estimated as usual.

L. DE K.

Analysis of Chrome Iron Ore. LOUIS DUPARC (*Ann. Chim. anal.*, 1904, 9, 201—203).—0.3 gram of chrome iron ore in impalpable powder is ignited with sodium carbonate in a platinum crucible for 8 hours. The mass is then removed from the crucible with hot water, and the liquid is evaporated with excess of hydrochloric acid to separate any silica. The filtrate from the silica is precipitated with ammonia, and the mixed hydroxides of iron, chromium, and aluminium are collected and ignited; the filtrate may be examined for calcium, &c.

The mixed oxides are then again ignited with sodium carbonate. The mass is boiled with water, which dissolves the chromium and aluminium as sodium salts, and leaves the iron oxide insoluble. The filtrate is cautiously acidified with nitric acid, the aluminium is precipitated with ammonia, and in the filtrate the chromic acid is estimated by precipitation with lead acetate; or it may be reduced by boiling with hydrochloric acid and then precipitated with ammonia.

L. DE K.

Detection of Nickel and Cobalt. STANLEY R. BENEDICT (*J. Amer. Chem. Soc.*, 1904, 26, 695—700).—*Detection of nickel only in the presence of cobalt.*—The solution is mixed with excess of sodium peroxide and heated to boiling. The precipitate is washed, and treated with a cold saturated solution of oxalic acid. To the filtrate are added a few drops of dilute solution of potassium ferricyanide, and then a slight excess of sodium hydroxide. A heavy black precipitate or a considerable darkening reveals the presence of nickel.

Detection of both metals in the presence of one another.—The mixed sulphides are oxidised with nitric acid, the excess of acid is expelled, and the residue dissolved in a little water. To 3 c.c. of the solution

are added 6—8 c.c. of aqueous sodium hydroxide, and the colour of the precipitate is observed. If cobalt is in excess the precipitate will have a dark blue colour; if nickel is present in very small amount the colour will not change within a few seconds to a bright pink, but if nickel is present in large amount the change of colour will be retarded for half an hour or more, and it will turn to a dirty grey. In the absence of nickel, the change of colour is practically instantaneous. If nickel is present in excess, the precipitate will not be a dark blue, but a somewhat bluish-green. If cobalt is absent, the colour will be a permanent pale-green.

L. DE K.

Estimation of Molybdenum in Steel Alloys. FREDERICK VAN DYKE CRUSER and EDMUND H. MILLER (*J. Amer. Chem. Soc.*, 1904, 26, 675—695).—The authors have arrived at the conclusion that the best method for the estimation of molybdenum in steel alloys is the sulphide separation. The sulphates, obtained in the usual way by treating the alloy with nitric and sulphuric acids, are dissolved in water containing sulphuric acid, the liquid is saturated with hydrogen sulphide, and then heated in a closed (pressure) bottle for 2 hours in the boiling water-bath. If the solution contains tungstic acid, its precipitation by hydrogen sulphide may be prevented by first adding some tartaric acid.

The molybdenum sulphide is washed and subjected to treatment with nitrohydrochloric and sulphuric acids. When copious sulphuric acid fumes appear, the mass is allowed to cool, then diluted with water, and any traces of iron oxide are precipitated by adding excess of ammonia. The filtrate is then mixed with excess of sulphuric acid, and the molybdenum estimated as usual by passing the solution through a zinc reductor and titrating with permanganate.

L. DE K.

Limit of Error in the Volumetric Estimation of Small Amounts of Gold. RALPH N. MAXSON (*Amer. J. Sci.*, 1904, [iv], 466—470. Compare Abstr., 1903, ii, 697).—A reply to Rupp (this vol., ii, 150). Whereas Rupp's process with arsenious acid is only applicable when the amount of gold is not less than a few milligrams, the titration process devised by Gooch and Morley can estimate with accuracy small fractions of a mg. of the metal. The aurous iodide formed in the reaction is sufficiently stable not to interfere with the estimation.

L. DE K.

Electrolytic Analysis with Rotating Electrodes. R. AMBERG (*Zeit. Elektrochem.*, 1904, 10, 385—386). **Electrolytic Precipitation of Palladium.** R. AMBERG (*Zeit. Elektrochem.*, 1904, 10, 386—387).—Palladium begins to be deposited in an acid solution of the chloride at 0.65 volt, but after a short time palladium peroxide comes down on the anode, the voltage rises to about 1.25, and spongy metal is deposited at the cathode. The same difficulties were encountered when alkaline or ammoniacal solutions were used. When an anode rotating some 600 to 650 times per minute is used, however,

no peroxide is formed, even with higher currents. The temperature is best kept at 60—65° and the voltage must not exceed the critical value of 1.25 volts. T. E.

Separation of Palladium in Mineral Acid Solution by Hydrazine. PAUL JANNASCH and L. ROSTOSKY (*Ber.*, 1904, 37, 2441—2461. Compare this vol., ii, 517, 519).—Hydrazine sulphate precipitates palladium quantitatively from hot mineral acid solutions, partly in the form of metal and partly as oxide. Palladium may thus be readily separated from the more electro-positive metals. In other cases, precipitation of the second metal may take place owing to the catalytic action of the precipitated palladium producing hydrogen in the active form of palladium hydride.

Palladium is separated from aluminium, chromium, uranium, molybdenum, and tungsten by the addition of a hot concentrated solution of hydrazine sulphate to the hot acid solution. The precipitate is dried and reduced in hydrogen. The separation from calcium, strontium, and barium is similar, except that in these cases the use of hydrazine hydrochloride, prepared from benzylideneazine or by saturating hydrazine hydrate with hydrogen chloride, is advisable.

The separation from manganese, cadmium, nickel, and cobalt by means of hydrazine sulphate is also complete, in spite of the existence of sparingly soluble double salts of these metals with hydrazine (Curtius and Schrader, *Abstr.*, 1895, ii, 10). In the case of nickel and cobalt, however, dilute solutions must be employed, and the precipitate must be thoroughly washed.

Owing to the secondary formation of hydrogen, copper is partially precipitated from hot solutions. A complete separation from palladium is possible by adding hydrazine hydrochloride to an ice-cold solution, previously diluted with alcohol. The separation of palladium from tin is effected in hot acid solution. The co-precipitation of antimony is prevented by the addition of citric acid. Arsenic is always partially precipitated from arsenious solutions, but the separation is complete in the case of arsenic acid.

The separation of palladium by this method from mercury, lead, bismuth, silver, platinum, or gold is not possible. None of these metals are precipitated by hydrazine salts alone, but the addition of a palladium salt, or of palladium black, causes precipitation owing to the production of hydrogen. The amount of precipitation varies with the time and with the quantity of the catalytic agent present. C. H. D.

Estimation of Palladium and its Separation from Other Metals by means of Acetylene. HUGO ERDMANN and O. MAKOWKA (*Ber.*, 1904, 37, 2694—2697).—The separation of palladium from other metals, such as copper, is not possible by means of Jannasch's hydrazine method (Jannasch and Bettges, this vol., ii, 519; Jannasch and Rostosky, preceding abstract). By aid of acetylene, however, palladium can be separated from the commoner metals as well as from platinum, iridium, rhodium, and gold. When acetylene gas is passed through a strongly acid solution containing palladium and

other metals or when a solution of acetylene in water is added, a brown precipitate is deposited, which, on being heated, yields palladium. Experiments are quoted to show that a quantitative separation of palladium from copper may be effected by this method.

A. McK.

Estimation of Alcohol in very Dilute Solutions. MAURICE NICLOUX (*Ann. Chim. anal.*, 1904, 9, 214—218).—The author defends his dichromate process against Pozzi-Escot's criticism (this vol., ii, 450).

L. DE K.

Estimation of Glycerol in Urine. AUGUST HERRMANN (*Beitr. chem. Physiol. Path.*, 1904, 5, 422—431).—The Zeisel-Fanto method with some modifications, which are described, gives good results with mixtures of urine and glycerol. Urine shows a small yield, even though no glycerol is administered.

W. D. H.

Microchemical Detection of Sugars by means of Phenylhydrazine Acetate. EM. SENFT (*Monatsh.*, 1904, 25, 397—421).—Sugars are best detected under the microscope in the form of their osazones. The material to be examined is added to phenylhydrazine acetate in glycerol solution, made by mixing 1:10 glycerol solutions of phenylhydrazine hydrochloride and of sodium acetate. The preparation is examined immediately, and again after two days. In most cases, the formation of the osazone is only hastened, but better crystallisation may take place if the preparation is warmed for half an hour on the water-bath. If the osazone does not separate in characteristic crystals, it is dissolved in alcohol and the alcoholic solution evaporated. Osazone preparations are stable to potassium hydroxide or 60 per cent. chloral solution, and may be preserved in glycerol-gelatin.

G. Y.

Reactions with Resorcinol in Urine. HEINRICH ROSIN (*Zeit. physiol. Chem.*, 1904, 41, 549).—In connection with Adler's observations (this vol., ii, 372), reference is made to the modification of Seliwanoff's reaction previously introduced by the author (*Abstr.*, 1903, ii, 616).

A number of substances, in addition to lævulose, give a red coloration with Seliwanoff's reagent, but in most cases the colour does not persist.

J. J. S.

Estimation of Glycogen. EDUARD PFLÜGER (*Pflüger's Archiv*, 1904, 103, 169—170).—A short description of the author's method. One hundred grams of the freshly-minced organ are boiled for 2 hours with 100 c.c. of 60 per cent. potassium hydroxide. After cooling, 200 c.c. of sterilised water are added and 400 c.c. of 96 per cent. alcohol. The precipitate is collected on a filter, washed once with a mixture of potassium hydroxide, 15 per cent. (1 vol.), and 96 per cent. alcohol (2 vols.), then with 66 per cent. alcohol. The precipitate is dissolved in boiling water, the solution neutralised and filtered. Hydrochloric acid is then added to bring its percentage up

to 2.2, and inversion is accomplished in three hours. After cooling, the fluid is neutralised, filtered, and the sugar estimated by the polarimeter. The amount of sugar multiplied by 0.927 gives the amount of glycogen.

W. D. H.

Analytical Examination of Urine. ALFRED H. ALLEN and ARNOLD R. TANKARD (*Pharm. J.*, 1904, [iv], 19, 8, 9).—The following modifications of some of the methods in ordinary use are given, the aim being to simplify the processes in such a manner as not to affect their accuracy for medical purposes.

Chlorides.—From 10 to 20 c.c. of the sample of urine are treated with 2 c.c. of sulphuric acid, and, while the mixture is still warm, a cold saturated solution of potassium permanganate is added drop by drop until the pink colour no longer fades, or fades only very slowly. The mixture is then neutralised with sodium hydroxide, using litmus paper as indicator, diluted to 50 c.c., and titrated with silver nitrate solution after adding a little potassium chromate solution. In the case of very dilute and pale urines, the treatment with acid and permanganate may be omitted.

Uric acid.—(Bartley's method.) Fifty c.c. of urine are heated nearly to boiling with 5 c.c. of magnesia mixture and 10 c.c. of ammonia of sp. gr. 0.960. While quite hot, the solution is titrated with *N*/50 silver nitrate solution, using ammonium sulphide to ascertain the end of the reaction. A drop of the liquid is placed on a small disc of filter-paper, the edge of which is then touched with a drop of ammonium sulphide. One c.c. of *N*/50 silver nitrate is equivalent to 0.00336 gram of uric acid.

Phosphates.—Two solutions are required: an aqueous solution containing 35 grams of uranium acetate and 160 c.c. of acetic acid (B.P.) per litre, and one prepared by dissolving 10 grams of sodium acetate and 15 c.c. of acetic acid in water and diluting to 100 c.c. Twenty c.c. of the uranium reagent and 5 c.c. of the sodium acetate solution are heated nearly to boiling and the urine gradually added from a burette. The end of the reaction is reached when a drop of the liquid no longer produces a brown coloration with a little powdered potassium ferrocyanide previously placed on a white plate. The uranium acetate solution is standardised on a solution of pure sodium phosphate.

Albumin.—Minute traces of albumin may be detected by agitating the urine with a few crystals of sulphosalicylic acid, a turbidity or precipitate being formed should albumin be present, which is not affected by heat. Precipitates due to albumoses or peptones dissolve on heating and reappear on cooling.

W. P. S.

Indirect Estimation of Fat in Milk. ALBERT STEINMANN (*Ann. Chim. anal.*, 1904, 9, 218—220).—A description of a calculating machine adapted for Fleischmann's formula, in which the fat is calculated from the specific gravity and the percentage of total solids, or, reversedly, the solids from the sp. gr. and fat.

L. DE K.

Estimation of the Fat in Milk and also the Physico-chemical Constants of the Latter. G. MEILLÈRE (*J. Pharm. Chim.*, 1904, [vi], 19, 572—579).—Twenty-five c.c. of the milk are

rendered alkaline with ammonia and then shaken with from 22 to 55 c.c. of a mixture of 1000 c.c. of 75 per cent. alcohol and 1100 c.c. of pure ether. The ethereal layer is separated and 10 c.c. of light petroleum are added to it. This causes any non-fatty substances dissolved by the ether to separate out. The ethereal solution is now evaporated and the residue of fat weighed. The aqueous portion is used for the estimation of the non-fatty solids.

Determinations of the specific gravity, surface tension, and electrical conductivity, and estimations of casein and lactose, are also considered to be of use in ascertaining the purity of a sample of milk. These determinations should be made on the milk deprived of its fat, a centrifugal machine answering the latter purpose. W. P. S.

Rapid Estimation of Fat. A. P. BRYANT (*J. Amer. Chem. Soc.*, 1904, 26, 568—573).—Fat in food stuffs or vegetable products may be completely extracted in 2 hours by means of carbon tetrachloride. This solvent has also a great advantage over ether, light petroleum, carbon disulphide, &c., in not being inflammable, and it is inexpensive.

The author uses the Knorr extraction apparatus.

L. DE K.

Quantitative Electrolytic Precipitation of Copper. THEODORE W. RICHARDS and HAROLD BISBEE (*J. Amer. Chem. Soc.*, 1904, 26, 530—536).—If it is desired to precipitate copper in a coherent film suitable for careful washing and accurate weighing, it is necessary to decrease as much as possible the volume of the solution and to increase the surface of deposition, and this may be easily attained by spreading the concentrated solution in a thin film between two platinum electrodes. The author uses a pair of concentric platinum crucibles or dishes, the annular space between them serving to contain the film of electrolyte. The vessels are prevented from touching each other by a suitably shaped construction of fine glass rod.

As the deposition of the copper proceeds, the current must be diminished. This is conveniently and automatically effected by using a storage cell at 1.9 volts as the source of the electromotive force.

L. DE K.

Chinese Tallow-seed Oil. L. MYDDLETON NASH (*Analyst*, 1904, 29, 110—111).—This oil is obtained from the seeds of *Sapium sebiferum*. The seeds are first steamed, when vegetable tallow runs out, and then pressed to obtain the oil. The latter has a brown colour and "dries" in about 3 days. The following figures were obtained from an analysis of a sample: sp. gr., 0.9395 at 15.5°/15.5°; free fatty acids (as oleic), 3.1 per cent.; unsaponifiable matter, 0.44 per cent.; iodine value (Hübl), 160.7; insoluble fatty acids, 93.96 per cent.; saponification equivalent, 277; α_D about -4° in a 100 mm. tube; refractive index v_D , 1.4835 at 20°.

W. P. S.

Cod-liver Oil and Other Fish Oils. JOHN F. LIVERSEEGE (*Analyst*, 1904, 29, 210—214).—The analytical constants of a number of cod-liver oils are given and also those of other oils used as adulter-

ants of cod-liver oil. The latter included seal, shark, dugong, haddock, menhaden, whale, brusmer, hoi, and ling oils. As regards specific gravity, menhaden and haddock oils are slightly heavier than cod-liver oil, shark oil notably so (0.962), whilst whale, hoi, and dugong oils are below 0.920. At a temperature of 25°, the butyro-refractometer sharply distinguished most of these oils, menhaden and brusmer being the exceptions. The readings obtained were: seal, 72.7; shark, 87.3; dugong, 60.3; haddock, 84.0; menhaden, 80.7; whale, 65.0; brusmer, 75.0; hoi, 73.7; and ling, 74.0. The cod-liver oils gave values between 76.3 and 80.0. About 84 per cent. of unsaponifiable matter was yielded by the shark oil. This oil had a saponification value of 6.0, of which 2.2 was due to free acid. With the exception of the nitric acid test, the colour reactions were untrustworthy for detecting these oils in cod-liver oil.

W. P. S.

The Thermoleometer. An Apparatus for the Detection of Falsifications in Olive Oil and other Vegetable and Animal Oils. MASSIMO TORTELLI (*Chem. Centr.*, 1904, 1, 1424—1426; from *Boll. Chim. Farm.*, 43, 193—203).—A suitable apparatus to perform the Maumené test for oils. It consists of a vacuum-jacketed tube, and a thermometer so made as to serve as an efficient stirrer. Twenty c.c. of the oil and 5 c.c. of sulphuric acid of sp. gr. 1.8413 are introduced, and the rise in temperature is noticed. A table is given showing the effect on a number of oils.

L. DE K.

Saponification of Compound Oils. PONTUS H. CONRADSON (*J. Amer. Chem. Soc.*, 1904, 26, 672—675).—2.5—10 grams of the mixture of hydrocarbons and fatty oils are boiled with a definite volume of $N/2$ alcoholic potassium hydroxide in a silver flask connected with a Soxhlet tube filled with glass beads and attached to an Allihn upright condenser. The flask is supported by a tripod, on which are placed two asbestos blocks, a thinner under one and a thicker one with tapered holes cut out in the centre to fit the flask; between these is placed an iron ring on which rests a small iron plate fitting the somewhat concave shape of the bottom of the flask. A direct gas flame is used for the boiling.

When boiled for a sufficiently long time, the excess of alkali is determined by first adding phenolphthalein and a few c.c. in excess of $N/4$ hydrochloric acid. After boiling to expel any carbon dioxide, the liquid is then carefully titrated with $N/4$ potassium hydroxide.

L. DE K.

Estimation of Formaldehyde in the Atmosphere. H. HENRIET (*Compt. rend.*, 1904, 138, 1272—1274).—The air is filtered and passed through a U-tube, heated at 250°, and filled with fragments of glass wool mixed with mercury oxide, when the formaldehyde is oxidised to carbon dioxide, which is then absorbed in potash bulbs. The amount of carbon dioxide originally present in the air, as determined by a blank experiment, is subtracted from the observed increase in weight of the bulbs, and the difference corresponds with the formaldehyde.

The method has been tested by slowly volatilising known weights of trioxymethylene in a current of air, and found to give good results. Aromatic hydrocarbons, which, according to Gautier, are present in the air of towns, do not interfere with the determination. The proportion of formaldehyde in normal air varies between 2 and 6 grams per 100 cubic metres.
H. M. D.

Detection of Saccharin in Beverages. ANTOINE VILLIERS, LOUIS MAGNIER DE LA SOURCE, FERDINAND ROCQUES, and MARCEL FAYOLLE (*Chem. Centr.*, 1904, 1, 1457—1458; from *Rev. Chim. Appl.*, 7, 144—152).—The liquid freed from alcohol is slightly acidified with acetic acid and precipitated with lead acetate, the excess of which is then removed with sodium phosphate or sulphate. The filtrate is shaken three times with half the bulk of benzene, and, after evaporating this, the residue is dissolved in 10 c.c. of 10 per cent. sulphuric acid, and to the warm solution is added a solution of potassium permanganate until slightly pink; this destroys any salicylic or similar acid. The liquid is now again agitated thrice with benzene, and if the residue has a sweet taste, it is heated as usual with sodium hydroxide for three minutes at 270°, and the mass is then tested for any salicylic acid formed by the action of the alkali on the saccharin.
L. DE K.

Detection of Albumin in Urines. RENAULT (*Ann. Chim. anal.*, 1904, 9, 212—214).—When testing strongly acid or amphoteric urines for albumin by means of acetic acid, urates or oxalates may be mistaken for albumin. The author now proposes to first render the sample distinctly alkaline with sodium carbonate, and then to apply the test to the filtrate.
L. DE K.

An Albumin [in Urine] Soluble in Acetic Acid. GUSTAVE PATEIN (*J. Pharm. Chim.*, 1904, [vi], 19, 580—584).—The albumin previously found by the author in a sample of urine is not an albumose, since it is coagulated by heat and redissolves on the addition of acetic acid.
W. P. S.

Testing Colloids. EDMUND J. MILLS and ARCHIBALD GRAY (*J. Soc. Chem. Ind.*, 1904, 23, 526—528).—The method described consists in coating a standard cotton thread with a solution containing a known quantity of the colloid under examination, drawing it through a nozzle 0.5 mm. in diameter, drying it, and determining the modulus of elasticity of the coat. The value of this modulus is directly related to the stiffening power of the colloid. Brook's No. 12 white cotton was employed in the experiments, and was carefully singed before coating. The coated threads were allowed to dry completely at the ordinary temperature by hanging them up and attaching a weight of 18 grams at their lower ends. The apparatus consisted of a couple of blocks capable of being moved towards or from each other by means of a right and left screw working below them. Each block carried a length of glass tubing. A length of coated thread was placed with either end in the tubes, its length

measured, and the deflection caused by adding a given weight, and also the radius of the thread determined by a kathetometer. The formula for the modulus E in the case of a circular section (kilos. per sq. millimetre of section) is: $E = 1/12 \times P/s \times l^3/\pi r^4$, where P = weight (kilos.) attached; l = exposed length (millimetres) of thread; s = deflection produced; and r = radius of the thread. The value of the modulus for the thread alone was found to be 86.9, and this was deducted from all the observations. The colloids examined were potato starch, maize starch, and gum arabic. These were found to have the comparative elasticities of 3, 4, and 7 respectively. In the case of potato starch and gum arabic, this ratio was strictly proportional to their prices.

W. P. S.

Van Deen's Reaction. DIOSCORIDE VITALI (*Gazzetta*, 1904, 34, i, 348—358).—According to Tarugi (*Gazzetta*, 1903, ii, 216; this vol., ii, 220), van Deen's reaction is of no value for the detection of blood spots, since potassium thiocyanate gives the same reaction. The author shows, however, that the reactions in the two cases display marked differences, especially as regards their sensitiveness.

T. H. P.

Estimation of Soil Acidity. FLETCHER P. VEITCH (*J. Amer. Chem. Soc.*, 1904, 26, 637—662).—As a result of a lengthy investigation, the author proposes to estimate the water-soluble acidity and the negative acidity due to readily attacked silicates by means of the sodium chloride method, using a proper correcting factor. The total apparent acidity is then determined by the lime-water method, and by allowing for the acidity in the saline solution the acidity due to insoluble organic matter is obtained.

The degree of acidity by the improved lime-water process is estimated as follows: to three portions of soil, each consisting of as many grams as there are mgrms. of calcium oxide per c.c. in the lime-water, 50 c.c. of pure distilled water are added, and to the first is then added 10, to the second 20, and to the third 30 c.c. of the standard lime-water. After quickly drying on the steam-bath, the residues are transferred to stoppered Jena flasks containing 100 c.c. of water. After remaining overnight with occasional shaking, 50 c.c. are pipetted off, a few drops of phenolphthalein are added, and the liquid is boiled until a pink colour appears or until the volume is reduced to 5 c.c. Then with two portions of treated soil, one of which has been rendered alkaline by the lime-water and the other is still acid, as guides, three fresh portions of 10 grams each are taken and treated with lime-water as before, except that the amount added to a dish differs from that added to another by 1 or 2 c.c. The dried residue is then treated as directed. The smallest amount of lime-water, which still gives a decided pink colour, is taken to represent the acidity of the soil.

L. DE K.

General and Physical Chemistry.

Ultra-red Absorption Spectra of Organic Liquids. MAX IKLÉ (*Chem. Centr.*, 1904, ii, 15; from *Physikal. Zeit.*, 5, 271—277).—The liquids were contained between parallel plates of fluorspar separated by a glass ring, special precautions being taken to prevent evaporation. The spectrum was obtained by means of a fluorite prism and zirconium light. The following groups of compounds were examined: (1) methylene chloride, chloroform, carbon tetrachloride; (2) methyl iodide, methylene iodide; (3) ethyl alcohol, ethyl bromide; and (4) ethyl alcohol and ethyl iodide. The results showed that the replacement of hydrogen or hydroxyl by a halogen increases the diathermancy of the liquid for all portions of the ultra-red spectrum, the effect, as a rule, being most marked for wave-lengths of the least diathermancy. The ultra-red absorption spectra of isomeric liquids did not show any general characteristics or relationship. All the compounds were least diathermanous for wave-lengths of 3435—3240 $\mu\mu$. Julius found that hydrocarbons also showed the same minimum, and attributed the phenomenon to the presence of the radicle C_nH_{2n+1} . Since carbon disulphide, however, behaves in the same way, the cause is possibly to be found in the carbon atom itself. Most compounds also give minima at 5—5.2 μ , whilst others show different characteristic minima. Maxwell's law does not hold for any of the liquids examined.

E. W. W.

The Spectrum of Calcium Fluoride in the Electric Arc. CHARLES FABRY (*Compt. rend.*, 1904, 138, 1581—1584).—When an electric arc is formed between cups containing calcium, strontium, or barium fluoride, there is formed, in addition to the spectrum of the metal, a very brilliant band spectrum due to the existence of the vaporised salt incompletely dissociated. In the case of calcium fluoride, the bands belong to two different types, but have common characteristics. All the bands are represented by the equation $N = B - Am^2$, where N is the inverse of the wave-length in a vacuum, and m a whole number which is greater than a certain limit in one type, and less than a certain limit in the other.

M. A. W.

[Phosphorescence of] **Kunzite.** CHARLES BASKERVILLE and GEORGE F. KUNZ (*Amer. J. Sci.*, 1904, [iv], 18, 25—28).—Kunzite, the new variety of spodumene, becomes luminescent when heated, but not when rubbed. An oscillating electric current, ultra-violet rays, Röntgen rays, and the emanations of radium and actinium all produce a brilliant orange-pink glow, which persists for some time after the exciting cause has been withdrawn. In its behaviour in this respect, kunzite differs from the hiddenite variety of spodumene, as well as from all other minerals.

L. J. S.

Emanations and Radiations. MARCELLIN BERTHELOT (*Compt. rend.*, 1904, 138, 1553—1555).—The author urges the importance of exact analyses of emanations before definite hypotheses regarding their nature are advanced.
M. A. W.

Influence of Changes of Temperature on Radioactive Substances. STEFAN MEYER and EGON R. VON SCHWEIDLER (*Chem. Centr.*, 1904, ii, 78; from *Physikal. Zeit.*, 5, 319—320).—Measurements of the velocity of discharge, made by means of an Elster-Geitel electroscope, have shown that in the case of uranium, uranium nitrate crystals, uranium nitrate solution, pitchblende, polonium, and radium, the velocity decreases with rise of temperature. This effect can only be explained by assuming that the activity is merely temporarily affected; the emanations may be increased, and the discharging power consequently decreased. In the case of radium and pitchblende, the activity of the β -rays is the most affected, whilst radiotellurium, which emits α -rays, is the least influenced by change of temperature.
E. W. W.

Action of Magnetic or Electric Forces on the Ponderable Emanation; Displacement of this Emanation by Air in Motion. R. BLONDLOT (*Compt. rend.*, 1904, 138, 1676—1679. Compare this vol., ii, 531).—Two similar bar magnets, encased in lead foil and in glass vessels, are placed parallel to one another on a table at a distance of 6 cm., the N pole of one being adjacent to the S pole of the other and projecting over the edge of the table; a 5 franc piece is placed just above the NS field thus formed, and the space below is explored by means of a small phosphorescent screen, with the results that in the absence of the magnets the emanation from the coin falls vertically, whilst in the presence of the magnets it is separated into three parts, one falling vertically, and two others equally inclined to the vertical on each side. Of these two latter, one is repelled by a negatively, and the other by a positively electrified body. These facts are readily explained on the assumption that the emanation from the coin consists of three kinds of particles, non-electrified, positively, and negatively electrified respectively. A current of air has the effect of diverting the path of the emanation. The emanation has an effect similar to that of the n -rays on a small electric spark.
M. A. W.

Action of Anæsthetics on the Sources of n -Rays (*Compt. rend.*, 1904, 138, 1159—1161). **Simultaneous Emission of n - and n_1 -Rays** (*ibid.*, 1332—1335). **The Anæsthesia of Metals** (*ibid.*, 1415—1418). **Contribution to the Study of n - and n_1 -Rays** (*ibid.*, 1486—1489). **Action of a Magnetic Field on n - and n_1 -Rays** (*ibid.*, 1586—1589). **Comparable Effects of β -Rays and n -Rays, or of α -Rays and n_1 -Rays, on a Phosphorescent Surface.** JEAN BECQUEREL (*Compt. rend.*, 1904, 139, 40—42).—According to the author's hypothesis, the cause of the Blondlot rays is to be found in the molecular vibration set up in a substance which becomes a source of n - or n_1 -rays when it suffers compression or expansion respectively; the vibratory movement

gives rise to perturbations of the ether analogous to light, which have the power of transmitting to a surface capable of absorbing them (for example, calcium sulphide, metals, &c.) the mechanical effect to which they owe their origin, these surfaces thereby becoming secondary sources of similar rays. The simultaneous emission of n -rays normally, and n_1 -rays tangentially, by the same substance is probably due to the mechanical deformation of the substance setting up a contraction in one direction and an expansion in another, for if a prism or cylinder is compressed in the direction of its axis it expands in a direction at right angles, and whilst n -rays are emitted normally to the base, n_1 -rays arise tangentially; further, Prince Rupert drops are elongated in the direction of their length and contracted normally to their surface; they form therefore a powerful source of n - or n_1 -rays according as the rays issuing normally to the surface or from the point are under investigation.

The power of emitting Blondlot rays is suspended by the action of alcohol or such anaesthetics as chloroform, ether, or nitrogen monoxide (compare Meyer, *Compt. rend.*, 1904, 138, 101), and metals which are normally transparent to the rays become opaque in the vapour of the same substances.

The undulatory movement, analogous to light waves, is not, however, the only element of the Blondlot rays; there is, in addition, an "emanation" capable of being deflected in a magnetic field in the same manner as the β -rays of radium bromide or a uranium salt. Further, the β -rays of a radioactive substance produce on a calcium sulphide screen an exactly similar effect to that produced by a source of n -rays, whilst the α -rays of poloniferous bismuth oxide have the same effect as n_1 -rays.

M. A. W.

Influence of the Colours of Luminous Sources on their Sensitiveness to n -Rays. C. GUTTON (*Compt. rend.*, 1904, 138, 1592—1593).—The author finds that when a ground glass screen is illuminated with simple colours obtained spectroscopically and exposed to a source of n -rays, it becomes more luminous when the colour of the light is violet or blue, slightly more luminous when the colour is green, whilst for yellow, red, or orange light there is no effect. This explains why calcium sulphide, with a violet phosphorescence, is more sensitive to the action of n -rays than the sulphides of the alkali earths and of zinc, which have a green or orange phosphorescence.

M. A. W.

A Photographic Method of Studying the Action of n -Rays on Phosphorescence. E. ROTHÉ (*Compt. rend.*, 1904, 138, 1589—1591).—The author describes a photographic method of rendering objective the effect of n -rays on a phosphorescent calcium sulphide screen. The method consists in taking a series of photographic impressions of a small, circular phosphorescent calcium sulphide screen at equal intervals of 20 seconds, the distance between the screen and the photographic plate being about 5 mm.; a curve constructed with the time intervals as abscissæ, and the diameters of the black spots which

constitute the photographic impressions as ordinates, is quite regular and represents the normal diminution of the phosphorescence with time. If, however, a similar series of photographic impressions are taken, the screen being subjected periodically to the action of heat rays or n - or n_1 -rays, which tend to increase or diminish the phosphorescence, the curve ceases to be regular, and the breaks in a curve so obtained can be taken as evidence of the presence of some perturbing source.

M. A. W.

Improvements in the Photographic Method for Recording the Action of n -Rays on a Small Electric Spark. R. BLONDLOT (*Compt. rend.*, 1904, 138, 1675—1676).—The author has previously described in detail a method for recording photographically the effect of n -rays on a small electric spark (compare *Compt. rend.*, 1904, 138, 453—456). In the present paper, a few improvements on the method are suggested, relating chiefly to the concentration of the n -rays by means of an aluminium lens.

M. A. W.

A New Method of Observing n -Rays and Analogous Agents. R. BLONDLOT (*Compt. rend.*, 1904, 139, 114—115).—The difficulty and fatigue attending the observation of n -rays and ponderable emanations (compare this vol., ii, 531, 602) by observing a change in the brightness of a phosphorescent ray on a dark surface is obviated by the following device: the calcium sulphide is deposited in the form of a band 0.001 to 0.002 metre wide, and 0.02 to 0.03 metre long, on a piece of white grained cardboard which is illuminated with a yellow light of such intensity that it forms with the blue phosphorescence of the calcium sulphide an almost white light which cannot be distinguished from the yellow light of the rest of the cardboard; if now a source of n -rays or an analogous agent be brought near the screen, the blue phosphorescence of the calcium sulphide is immediately visible; and, conversely, if the blue phosphorescence is just visible, the action of n_1 -rays causes it to disappear.

M. A. W.

Dielectric Cohesion of Saturated Mercury Vapour and its Mixtures. E. BOUTY (*Compt. rend.*, 1904, 138, 1691—1692. Compare this vol., ii, 309).—In view of the high density of mercury vapour, its dielectric cohesion is very small, being only 0.85 of that of air, and the addition of other gases, such as carbon dioxide or hydrogen, causes a marked increase in the value; in these respects mercury resembles argon. The dielectric cohesion of a mixture of the two monatomic gases, mercury vapour and argon, however, is very much greater than the calculated value, showing that mercury has the same effect as the polyatomic gases in increasing the dielectric cohesion of argon.

M. A. W.

Electrical Resistance of Lead Peroxide. FRANZ STREINTZ (*Zeit. Elektrochem.*, 1904, 10, 414—415).—A bar of lead peroxide formed by compressing the powdered substance always contains small cracks which increase its electrical resistance.

A more serious error is due to transition resistances between the

lead peroxide and the metallic terminals. In a measurement the details of which are given, the transition resistances amounted to nearly three-quarters of the apparent resistance of the bar.

The transition resistance between lead and lead peroxide is especially large, hence Ferchland's result (*Zeit. Elektrochem.*, 1903, 9, 670) is probably much too high. The author regards his own result (specific resistance = 0.000223 ohm) (*Abstr.*, 1903, ii, 127) as an upper limit.

T. E.

Electrolysis with Rapidly Moving Electrodes. HENRY SAND (*Zeit. Elektrochem.*, 1904, 10, 452—454).—With reference to Amberg's paper on the advantages of rotating electrodes in electrolytic analysis (this vol., ii, 593), the author points out that the theoretical explanation of these advantages is contained in his paper on the electrolysis of solutions of copper sulphate (*Abstr.*, 1901, ii, 82). The rapid circulation of the liquid keeps up the supply of ions at the electrodes and so permits a metal to be deposited much faster than would be the case if diffusion alone were depended on.

T. E.

Heat of Transformation of Black Crystallised Antimony Sulphide into the Orange Precipitated Sulphide. MARCELLIN BERTHELOT (*Compt. rend.*, 1904, 139, 97—98).—A reply to Guinchant and Chrétien (compare this vol., ii, 568). The author maintains his original conclusion (compare *Ann. Chim. Phys.*, 1887, [vi], 10, 136) that for dilute solutions and constant temperatures the heat of conversion of black crystallised antimony sulphide into the orange variety is nil.

M. A. W.

Thermochemical Studies. DANIEL LAGERLÖF (*J. pr. Chem.*, 1904, [ii], 69, 513—544. Compare this vol., ii, 382).—A continuation of the author's criticism of Thomsen's theory of the heat of formation of carbon compounds.

G. Y.

Heat of Combustion of Organic Compounds. JULIUS THOMSEN (*Zeit. anorg. Chem.*, 1904, 40, 185—195).—A criticism of Lemoult's results (*Abstr.*, 1903, ii, 410; this vol., ii, 12, 310). The theory respecting the heat of combustion of hydrocarbons advanced by Lemoult, namely, that the heat of combustion of a hydrocarbon is dependent only on the number of hydrogen atoms contained in the molecule of the hydrocarbon and on the number of linkings between the carbon atoms in the molecule, is not a new contribution to the theory of the heat of combustion of organic compounds. The chief error made by Lemoult consists in his calculating the heat of combustion of any particular hydrocarbon irrespective of whether the hydrocarbon in question is solid, liquid, or gaseous. The constants for hydrocarbons in the solid or liquid forms are always greater than those for hydrocarbons in the gaseous form. Many of the values quoted by Lemoult are very inaccurate.

A. McK.

Heat of Combustion of Organic Compounds containing Sulphur. Remarks relating to Halogen Compounds. PAUL LEMOULT (*Compt. rend.*, 1904, 139, 131—134. Compare *Abstr.*, 1903, ii, 410; this vol., ii, 12, 310, 382).—The heat of combustion of the

compound $C_xH_{y-a}(N_mH_a)O_pS_n$, as calculated from the expression $102x + 55/2y + (16.5m - 10a) - \Sigma p\phi + 151n$, the value of ϕ varying with state of combination of the oxygen in the molecule, agrees closely with the experimental value. The heats of combustion of organic compounds containing halogens can be calculated from the general formula given above, making the correction of -15.5 Cal. for each atom of chlorine, -0.5 Cal. for each atom of bromine, or 9.5 Cal. for each atom of iodine.

M. A. W.

Heat of Vaporisation of Aniline. WLADIMIR F. LUGININ (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 672—679).—The author replies to the criticisms of Kurbatoff (compare Abstr., 1903, i, 246), who obtained values $2\frac{1}{2}$ per cent. greater than that given by the author (Abstr., 1901, ii, 145; 1903, ii, 7) for the heat of evaporation of aniline. Further measurements of this magnitude yield the values 104.09, 103.57, and 104.49, having the mean 104.04, which agrees well with the number (104.0) previously given by the author (*loc. cit.*).

T. H. P.

The Molecular Volume of Solid Compounds and the Relation of the Osmotic Pressure to the Depression of the Freezing Point and the Raising of the Boiling Point of Solutions. WILHELM VAUBEL (*J. pr. Chem.*, 1904, [ii], 69, 545—559. Compare Traube, Abstr., 1896, ii, 153; Longinescu, this vol., ii, 112).—The author shows that for 18 liquids, the boiling point of any solvent is raised to approximately the same extent for one gram-molecule of solute per gram-molecule of solvent. This effect is calculated, in terms of heat, from the relation $E = 3.15C_L(m + m_1)$ cal., where m and m_1 are the gram-molecules of solute and solvent respectively and C_L is the specific heat of the solution.

The depression of the freezing point (15 solvents) due to one gram-molecule of solute per gram-molecule of solvent varies from 105 for water to 17.2 for palmitic acid. As, in the series of fatty acids, the tendency to form large molecules diminishes as the carbon chain increases, palmitic acid may be considered to be unassociated, in which case 17.2 is the true molecular depression. The state of aggregation of other solvents, in the solid state, is found by dividing the observed molecular depression by 17.2. Thus the solid molecule of water, $105/17.2 = 6.1$, is $(H_2O)_6$. The heat rendered latent by the solution of one gram-molecule of solute per gram-molecule of solvent is

$$17.2.C_L(m + m_1) \text{ cal.}$$

When a substance is dissolved in water, it enters into reaction with the complex $(H_2O)_6$, forming $(H_2O)_5M$, and setting $1H_2O$ free. This molecule of water, acting as a gas molecule, produces the effect of osmotic pressure, which approximates to the pressure equivalent to the rise in the boiling point. The depression of the freezing point of a solution is due to the molecule dissolved as well as to the water molecule set at liberty; the raising of the boiling point is an effect of the latter only. The energy rendered latent by solution of a substance

near the freezing point of the solvent is equivalent to a pressure of 227.6 atmospheres, that at the boiling point to 63 atmospheres.

G. Y.

Internal Friction of Solutions. GEORGE RUDORF (*Zeit. Elektrochem.*, 1904, 10, 473—474).—In a previous paper (Abstr., 1903, ii, 404) the author found that carbamide lowers the internal friction of water. Fawsitt (this vol., ii, 323) has failed to confirm this result. Rudorf now states that his experiments were made with a coiled capillary tube, the shape of which caused the results to be affected by a systematic error. Fawsitt's results agree with the formula $\eta = 1 + an$ for fairly dilute solutions. Some experiments on solutions of two substances are in agreement with Fawsitt's rule that the internal friction of a solution of several substances is equal to the product of the frictions of the solutions of the single substances. T. E.

Velocity of Reaction in Aqueous Solutions near the Point of Maximum Density. ANTONIO QUARTAROLI (*Gazzetta*, 1904, 34, i, 505—516).—The author has measured the velocities of hydrolysis of methyl and ethyl acetates by sodium hydroxide, first at low temperatures and for small intervals of temperature, and then after having artificially lowered the point of maximum density of the water by the addition of methyl or ethyl alcohol. The results show that none of the formulæ suggested for expressing the variation of the velocity of reaction with the temperature represents satisfactorily the changes in the velocity of hydrolysis of methyl and ethyl acetates in aqueous solution between 10° and 0°, whilst the changes at higher temperatures or in solutions containing more than 10 per cent. of methyl or ethyl alcohol are expressed moderately well by these formulæ. T. H. P.

Order of Magnitude of the Time of Formation of Complex Molecules, Equilibrium Constants, and Atomic Dimensions. FRITZ HABER (*Zeit. Elektrochem.*, 1904, 10, 433—436).—The concentrations of ions in solutions, calculated from measurements of *E.M.F.*, are often very small. Assuming the dimensions of an atom given by the kinetic theory, the author calculates, for example, that a certain solution containing $\text{Ag}(\text{CN})_3$ ions contains only 8 silver ions in a litre.

Ostwald has suggested that the equilibrium constant is to be interpreted as the ratio between the times which a silver atom passes in the ionic condition and in the condition of a complex ion. This is the same thing as the ratio between the times required to form a molecule of the complex ion from, and the time required to decompose it into, its constituent ions. Since all the silver can be precipitated (by a metal or electrolytically) from the solution under consideration in a short time, it follows that the time required to decompose the complex ion is small; from the equilibrium constant, it is seen that the time required for the combination of Ag^+ and $(\text{CN})^-$ ions is 10^{22} times smaller. Supposing that the combination merely required the passage of electricity across a space of atomic dimensions with the velocity of light, the time required would be at least 10^{-18} second.

If ponderable matter has to move, it is much greater. It appears, therefore, that Ostwald's suggestion leads to the assumption of reaction velocities thousands or millions of times greater than the greatest conceivable on the atomic hypothesis.

The author points out that the small ionic concentrations calculated are not necessarily realities. The potential of an electrode is determined by the reaction taking place at it, and this depends on the well-defined concentrations of the ions present in large quantity. For a silver electrode immersed in a solution containing Ag^+ , $\text{Ag}(\text{CN})_3^-$, and $(\text{CN})^-$ ions, the reaction is $\text{Ag} + 3(\text{CN})^- + F \rightleftharpoons \text{Ag}(\text{CN})_3^-$, and not necessarily $\text{Ag} + F \rightleftharpoons \text{Ag}^+$. T. E.

Systems containing Silicic and Hydrofluoric Acids. EMIL BAUR (*Zeit. physikal. Chem.*, 1904, 48, 483—503. Compare this vol., ii, 119).—As a preliminary to a dynamical study of the reaction between water and silicon fluoride, the vapour density of hydrofluosilicic acid has been determined at 23° , 31.5° , and 42° , and under pressures between 650 and 1350 mm. Hg. The molecular weight indicated under these conditions lies between 80 and 83, showing that hydrofluosilicic acid is probably dissociated to the extent of two-thirds or thereby (compare Thorpe and Hambly, *Trans.*, 1889, 55, 163).

With the equilibrium between silicon fluoride, hydrofluoric acid, water, and silicic acid, the composition of the vapour given off from a dilute solution of hydrofluosilicic acid containing free silicic acid is closely allied. When a 13.3 per cent. solution of hydrofluosilicic acid in water is boiled under a pressure of 720 mm., the vapour contains the molecules HF and SiF_4 in the numerical ratio 2:1. The vapour given off on boiling a more concentrated solution contains relatively more silicon fluoride, that from a more dilute solution contains relatively more hydrofluoric acid. The equilibrium constant of the reaction $\text{SiO}_2 + 4\text{HF} = \text{SiF}_4 + 2\text{H}_2\text{O}$ has been determined at 104° and 270° and found to have the respective values 163×10^7 and 540×10^5 . From these numbers, it follows that the equilibrium point of the foregoing reaction shifts to the left with rising temperature. Hence the formation of silicon fluoride and water from silicic and hydrofluoric acids is accompanied by the evolution of heat, and from the equation $d(\log_e K)/dT = q/RT^2$, the heat evolution q is calculated to be 8945 cal. This is only about one-third of the value calculated from thermochemical data, but the latter are probably inaccurate. J. C. P.

Reduction of Nitro-compounds by Stannous Haloids. HEINRICH GOLDSCHMIDT and KRISTIAN INGEBRECHTSEN (*Zeit. physikal. Chem.*, 1904, 48, 435—466).—A quantitative study has been made (1) of the reducing action of stannous chloride and hydrochloric acid on *m*-nitrobenzenesulphonic acid, *p*-nitrotoluenesulphonic acid, *o*- and *m*-nitrobenzoic acids, *o*-, *m*-, and *p*-nitroanilines, 3-nitro-4-toluidine, 2-nitro-4-toluidine, 4-nitro-2-toluidine, 5-nitro-2-toluidine, 6-nitro-2-toluidine; (2) of the reducing action of stannous bromide and hydrobromic acid on *m*-nitrobenzenesulphonic acid, *m*-nitrobenzoic acid, 2-nitro-4-toluidine, *p*-nitrophenol. Series of experiments in which the acid concentration remained the same showed that so far as the

stannous salt and the nitro-compound are concerned the reaction is of the second order. This means that a nitroso-compound is primarily formed, which is then further reduced with very great velocity. It can indeed be shown that a nitroso-compound is reduced practically instantaneously by acid stannous chloride. When the reduction of a nitro-compound in presence of varying amounts of hydrochloric acid is studied, it is found that the rate of change is directly proportional to the concentration of the acid. The authors consider that the only way of interpreting this result is to adopt Young's view (Abstr., 1901, ii, 318; compare Noyes, Abstr., 1902, ii, 498) that an acid solution of stannous chloride contains the complex SnCl_3H , with its ions H^+ and SnCl_3' . On the supposition that the ion SnCl_3' is the active agent in the reduction, it is possible to formulate satisfactorily the course of the change. The governing equation is thus found to be $dx/dt = k(a-x)(b-x)(c-x)$, where a , b , and c are the initial concentrations of nitro-compound, stannous chloride, and hydrochloric acid respectively. Hence, if c is large compared with a and b , the reaction is of the second order, in agreement with the experiments. Although the potential difference $\text{Pt} \mid \text{SnCl}_2, \text{HCl}$ is practically the same as the potential difference $\text{Pt} \mid \text{SnBr}_2, \text{HBr}$, the velocity constant of reduction with stannous bromide and hydrobromic acid is 8 times as great as that with stannous chloride and hydrochloric acid. This is to be attributed to the different oxidisability of the ions SnBr_3' and SnCl_3' , or to the different equilibrium between these ions and their corresponding molecular complexes. Whether the chloride or bromide is used as the reducing agent, a rise of 10° means a doubling of the velocity constant.

The effect of hydrochloric acid on the reduction appears to be exceptional in the case of *o*-nitroaniline and 3-nitro-4-toluidine, but this is to be attributed to the relative weakness of nitrated aromatic bases, in which the nitro-group occupies the ortho-position relatively to the amino-group (compare Loewenherz, Abstr., 1898, ii, 326). Special consideration of these two cases makes it probable that in the case of the nitro-bases it is the positive basic ions that are primarily involved in the reaction.

When the rates of reduction of isomeric compounds are compared, it is found that the velocity is greatest for the orthonitro-compound; this rule holds only when the nitro-group occupies the ortho-position relatively to the characteristic group ($\text{CO}_2\text{H}, \text{NH}_2$) of the compound, but not when the nitro- and methyl groups are next each other. In general, the velocity of reduction of a nitro-compound is diminished by the introduction of a methyl group. J. C. P.

Catalytic Action of Metallic Chlorides. HEINRICH GOLDSCHMIDT and HALFDAN LARSEN (*Zeit. physikal. Chem.*, 1904, 48, 424—434. Compare Bruner, Abstr., 1902, ii, 447; Slatore, Trans., 1903, 83, 729).—The influence of stannic chloride and aluminium chloride on the rate of chlorination of nitrobenzene has been studied quantitatively. Solutions of chlorine in nitrobenzene and of the metallic chloride in nitrobenzene were mixed and kept in a bath at a suitable temperature, the amount of free chlorine being determined

from time to time by adding a known quantity of the mixture to excess of potassium iodide solution. For a given quantity of catalytic agent, the course of the chlorination is that of a unimolecular reaction. The rate of change is proportional to the concentration C of the catalytic agent, and is therefore expressed by the equation $dx/dt = K.C(a-x)$. At 50° , K , for stannic chloride, $= 0.000778$, for aluminium chloride $K = 0.0239$, so that the chlorination of nitrobenzene takes place 31 times more rapidly in the presence of aluminium chloride than in that of stannic chloride. Over the temperature range $50-100^\circ$, the velocity constant at $T+10$ is 1.35 times that at T . Comparative experiments show that ferric chloride is still more effective than aluminium chloride. Antimony and phosphorus pentachlorides and arsenic trichloride exert practically no catalytic action.

Friedel and Craft's reaction also has been studied quantitatively, and in particular the interaction of benzyl chloride, anisole, and aluminium chloride. The course of the reaction was followed by extracting the unchanged benzyl chloride, hydrolysing with alcoholic soda, and titrating with silver nitrate. Experiments at 25° , 15.2° , and 0° show that the reaction between anisole and benzyl chloride is of the first order, and that the rate of change is proportional to the concentration of the aluminium chloride. For a rise of 10° , the velocity coefficient is nearly doubled.

J. C. P.

Passivity of Metals. WOLF JOHANNES MÜLLER (*Zeit. physikal. Chem.*, 1904, 48, 577—584).—When the conception of electrons is applied to the phenomena of passivity, it becomes probable that Schönbein's view is correct, and that the explanation which refers the passivity to the presence of a non-metallic layer is incorrect. It also follows that every metal which can form ions of more than one valency should exhibit activity or passivity under suitable conditions. The behaviour of chromium, lead, and iron is completely in harmony with this view, as is also the behaviour of platinum under the action of an alternating current (compare Ruer, *ibid.*, 1900, 34, 81).

J. C. P.

Spontaneous Crystallisation of Supercooled Liquids. CHRISTIAN FÜCHTBAUER (*Zeit. physikal. Chem.*, 1904, 48, 549—568).—Partly a theoretical paper on the limits of stability of supercooled liquids.

In the case of liquids dissolved in liquids, supersaturation is impossible, and this appears to be conditioned by the presence of dust particles. That these are immediately effective in preventing supersaturation in liquids, but effective only after a certain degree of supersaturation in the case of crystalline substances, indicates that these dust particles are amorphous, and consist probably of some widely distributed colloid (say silica).

J. C. P.

Crystallisation of Glassy Masses. W. GUERTLER (*Zeit. anorg. Chem.*, 1904, 40, 268—279).—Tamman has shown that a large number of substances can be supercooled and retained in an unstable, amorphous condition if the range of temperature of maximum sponta-

neous crystallisation and maximum rate of crystallisation is quickly passed through.

Sodium silicate, Na_2SiO_3 , cobalt pyroborate, $\text{Co}_2\text{B}_2\text{O}_5$, copper metaborate, CuB_2O_4 , and manganese diborate, MnB_4O_7 , when melted and quickly cooled, solidify to a clear glass. Such glasses were gradually heated, the temperature being measured by a Le Chatelier thermometer, and the temperatures noted at which the crystallisation took place. The crystallisation in each case was, of course, accompanied by a considerable rise of temperature. The results are represented by curves.

The temperature at which crystallisation begins is independent of the rate of heating; this is shown most clearly in the experiments with sodium metasilicate. A. McK.

Velocity of Crystallisation of Fused Liquid Mixtures. FRIEDRICH DREYER (*Zeit. physikal. Chem.*, 1904, 48, 467—482).—It has been shown by Tammann and others that when the velocity of crystallisation is plotted against the bath temperature the curve obtained has a rising branch, a maximum, and then a falling branch, as the temperature is lowered. The author shows that at temperatures corresponding with the falling portion of the curve the velocity of crystallisation of formanilide is sometimes increased, sometimes diminished, by the addition of other substances. On the rising branch of the curve, addition of other substances invariably leads to a diminution of the velocity of crystallisation, a diminution which cannot be entirely accounted for by the lower temperature prevailing at the crystallising face. As the concentration of the added substance increases, so the maximum of the above-mentioned curve for formanilide shifts to lower temperatures. J. C. P.

Excelsior Condenser. Excelsior Distillation Column. HENRI VIGREUX (*Chem. Zeit.*, 1904, 28, 686).—In the condenser described, the inner tube has a series of indentations lying closely together and each carried nearly across the tube, so that there is a large condensing surface. In a condenser 30 cm. long, the vapour from $\frac{1}{2}$ litre of ether in rapid ebullition is completely condensed. At the same time, any moisture carried mechanically to the condenser tube is prevented from passing on.

A fractionating column on the same principle is described and illustrated. A. McK.

New Wash-bottle. EDUARD KOB (*Chem. Zeit.*, 1904, 28, 687).—In the arrangement described, instead of the doubly-perforated cork of the ordinary wash-bottle, only one perforation of the cork is necessary, since the tube passing through it to the bottom of the flask is partitioned, and one side connected with the outlet, the other with the inlet tube. A. McK.

Black Coating Resisting Acids and Alkalis. FERDINAND JEAN (*Ann. Chim. anal.*, 1904, 9, 258).—Laboratory benches, &c., are treated three times in succession with (1) solution of 150 grams of aniline

hydrochloride per litre, (2) a solution containing 86 grams of cupric chloride, 77 grams of potassium chlorate, and 33 grams of ammonium chloride per litre.

After 8 days, a coating of linseed oil is put on. L. DE K.

Inorganic Chemistry.

Hypochlorous Acid. Electromotive Behaviour. WALTHER NERNST and JULIUS SAND (*Zeit. physikal. Chem.*, 1904, 48, 601—609).—With the help of Jakowkin's study of the equilibrium between chlorine and water, it is possible to calculate the potential difference between a platinum electrode and solutions containing hypochlorous acid or hypochlorites. When the concentration of the hypochlorous acid is not too small, there is exact agreement between theory and experiment, and the platinum electrode is apparently polarised by the oxygen produced in the primary decomposition of the HClO molecule. In this and kindred investigations it is necessary to make sure that the substance which is primarily responsible for the polarisation of the electrode is present in sufficient concentration. Other analogous cases are furnished by the polarisation of platinum in ozone and nitric acid solutions. J. C. P.

Strength of Hypochlorous Acid. JULIUS SAND (*Zeit. physikal. Chem.*, 1904, 48, 610—614).—A solution of sodium hypochlorite absorbs more carbon dioxide than pure water at the same temperature, and from the amount of this excess it is possible, when the dissociation constant of carbonic acid (Walker, Abstr., 1900, 268) is taken into account, to calculate the dissociation constant of hypochlorous acid. The value found, which is probably a little too high, is 3.7×10^{-8} at 17° . J. C. P.

Densities of Sulphur Dioxide and Oxygen. ADRIEN JAQUEROD and ALEXANDRE PINTZA (*Compt. rend.*, 1904, 139, 129—131).—The authors have determined the densities of sulphur dioxide and oxygen by means of the method used by Morley in determining the density of hydrogen (compare Abstr., 1895, ii, 261; 1896, ii, 595); a large vessel of known volume connected with a manometer was filled with the gas liberated from a small piece of apparatus, which was weighed before and after the experiment. In the case of oxygen, the gas was obtained by electrically heating potassium permanganate, whilst the sulphur dioxide was obtained from the liquid by lowering the pressure. The weight of a normal litre of oxygen as found by this method was 1.4292 grams with a maximum error of $1/3000$, and the corresponding value for sulphur dioxide was 2.92664 grams with a maximum error of $1/10000$; Leduc found 2.9267 (compare Abstr.,

1893, ii, 516). The weight of a litre of sulphur dioxide at 0° under 570 mm. pressure was found to be 2.18172 grams, and under 380 mm. pressure 1.44572 grams. M. A. W.

Action of Hydrogen Peroxide on Tellurium Dioxide. A New Method for the Preparation of Telluric Acid. ALEXANDER GUTBIER and W. WAGENKNECHT (*Zeit. anorg. Chem.*, 1904, 40, 260—263).—Potassium tellurate is produced when a 15 per cent. solution of hydrogen peroxide acts on a mixture of potassium hydroxide and tellurium dioxide at 60 – 70° . When the solution is acidified by sulphuric acid, telluric acid is precipitated and may be obtained free from potassium salts. Sodium hydroxide solution may be substituted for potassium hydroxide.

The telluric acid obtained was identified by analysis and by the following reactions. When boiled with hydrochloric acid, it evolved chlorine, a reaction characteristic of sexavalent tellurium. When heated in an ignition tube, water was evolved, the residue becoming orange-yellow and then melting to a white mass, which was soluble in hydrochloric acid to an amber-yellow solution. The silver and sodium salts were also prepared. A. McK.

Behaviour of Telluric Acid during Electrolysis. A New Modification of Colloidal Tellurium. ALEXANDER GUTBIER and F. RESENSCHECK (*Zeit. anorg. Chem.*, 1904, 40, 264—267).—When an aqueous solution of telluric acid containing potassium cyanide is electrolysed with a current of 0.5 ampere, the solution gradually becomes brownish-violet owing to the formation of tellurium in the hydrosol form; as the electrolysis is continued, the tellurium separates as a flocculent precipitate. When ammonium oxalate is substituted for potassium cyanide, the steel-blue hydrosol of tellurium is first of all formed. By dialysis, the new brownish-violet hydrosol form may be obtained in brilliantly-coloured solutions, which are not decomposed after six months. A. McK.

Reaction between Nitric Oxide and Oxygen at Low Temperatures. LUIGI FRANCESCONI and N. SCIACCA (*Gazzetta*, 1904, 34, i, 447—457).—The authors have made a number of experiments on the influence of temperature on the reaction between nitric oxide and oxygen, on the conditions under which the nitrous anhydride and nitrogen peroxide formed pass into one another under the action of nitric oxide or oxygen, and on the stability of nitrogen trioxide. The results arrived at are briefly as follows: (1) liquid nitric oxide and oxygen or gaseous oxygen and liquid or solid nitric oxide, or gaseous nitric oxide and liquid oxygen, mixed in all proportions, even with the oxygen in large excess, always yield nitrogen trioxide. (2) Gaseous nitric oxide and oxygen, the latter being in excess, also give nitrogen trioxide if they react at a temperature lower than -110° . (3) When subjected to the action of oxygen, nitrogen trioxide is transformed into nitrogen peroxide only at temperatures above -100° . (4) The reduction of nitrogen peroxide to nitrogen trioxide by nitric oxide commences at -150° . (5) Nitrogen trioxide is stable under the ordinary pressure up to a temperature of -21° . T. H. P.

Properties of Mixtures of Nitric and Sulphuric Acids. III. A. V. SAPOSCHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 669—671. See this vol., ii, 251, 558).—The author has determined the sp. gr. and specific conductivities of mixtures in varying proportions of nitric acid of sp. gr. 1.48 and sulphuric acid. A very small addition (5 per cent.) of nitric acid increases the conductivity of sulphuric acid ten times; this is due to the presence in the nitric acid of water, which produces the same effect.

T. H. P.

Preparation of Phosphorus Tribromide. ANASTASIOS K. CHRISTOMANOS (*Ber.*, 1904, 37, 2883).—Phosphorus tribromide is obtained (yield, 88 per cent.) by the action of bromine on yellow phosphorus under a layer of benzene.

G. Y.

Limits of Miscibility of Boric Anhydride and Borates in the Fused Condition. W. GUERTLER (*Zeit. anorg. Chem.*, 1904, 40, 225—253).—Many metallic oxides, when melted with an excess of boric anhydride at temperatures up to 1400°, form two layers, the upper of which contains in most cases almost pure boric anhydride, whilst the lower contains the liquid borate together with an excess of boric anhydride. The lower layers can almost always be induced to crystallise, when the crystalline borates separate, and may be obtained pure by washing with water.

Oxides, which dissolve in fused boric anhydride, are divided into three classes. I. Those oxides which with fused boric anhydride yield clear, homogeneous molten masses, from which, on cooling, the oxide again separates, or clear glasses are produced. The oxides of lithium, potassium, sodium, rubidium, calcium, thallium and silver are included in this class. II. Those oxides which with fused boric anhydride also yield clear, homogeneous molten masses, but when cooled form an emulsion. The behaviour in this case is similar to that of partially miscible liquids, like phenol and water. For mixtures of lead monoxide and boric anhydride, the temperatures at which for different concentrations the formation of emulsion began were determined. To this group belong cuprous oxide, antimony trioxide, arsenic trioxide, titanium dioxide, the oxides of lead and bismuth, and molybdenic, tungstic, and vanadic anhydrides. III. Oxides which form two layers with fused boric anhydride from the lower layer of which the borate can be separated. The metaborates of copper oxide, cerium oxide, neodymium oxide, praseodymium oxide, lanthanum oxide, gadolinium oxide, and samarium oxide, the pyroborates of magnesium oxide, cobaltous oxide, and nickelous oxide, and the diborates of calcium, strontium, and manganese were prepared by this method.

Burgess and Holt's results (*Proc.*, 1903, 19, 221) are criticised.

A. McK.

Electrolytic Reduction of Carbon Dioxide. ALFRED COEHN and STEFAN JAHN (*Ber.*, 1904, 37, 2836—2842. Compare Royer, *Compt. rend.*, 1870, 70, 731).—Carbon dioxide is reduced electrolytically in aqueous sodium hydrogen carbonate, or, better, potassium sulphate solutions, but not in sodium carbonate or acid solutions. With most cathodes, reduction takes place to a small extent. With a cathode of

zinc, freshly coated with zinc from a potassium cyanide bath, a 50 per cent. yield of formic acid is obtained. Repeated use of an amalgamated zinc cathode results at first in increased yields (up to 82 per cent.), but the cathode suddenly loses its activity. Amalgamated copper cathodes give constant yields (45—50 per cent.) on repeated use. After prolonged electrolysis of carbon dioxide in potassium sulphate solution, comparison of the acidity of the mixed cathode and anode solutions with the potassium permanganate titre shows the reduction to result in the formation of formic acid with little or no formaldehyde. Formic acid can also be obtained by electrolysis of an aqueous solution of carbon dioxide. G. Y.

Bell Process of Electrolysing Aqueous Solutions of Alkali Chlorides. G. ADOLPH (*Zeit. Elektrochem.*, 1904, 10, 449—450).—A claim for priority against Steiner (this vol., ii, 483). T. E.

Preparation of Sodium and Calcium Hyposulphites by Electrolysis. ALBERT R. FRANK (*Zeit. Elektrochem.*, 1904, 10, 450—452).—In reply to criticism by Elbs and Becker (this vol., ii, 556), the author states that in the preparation of solutions of sodium hyposulphite by electrolysis of solutions of sodium hydrogen sulphite it is necessary to use an almost neutral solution. The presence of free sulphurous acid liberates hyposulphurous acid, which readily decomposes. If this precaution is taken and the current density gradually increased, a good current efficiency can be maintained for a much longer time, and solutions containing 30 to 40 grams of hyposulphite per litre obtained.

Solutions of calcium hydrogen sulphite containing up to 90 grams of the salt per litre are employed in large quantities in the preparation of cellulose, and Elbs and Becker are mistaken in saying that the maximum solubility is 9.3 grams per litre. When a nearly neutral solution of calcium hydrogen sulphite containing from 40 to 60 grams of SO_2 per litre is electrolysed, the calcium hyposulphite soon begins to crystallise out in silky needles. From 30 to 40 per cent. of the weight of the calcium hydrogen sulphite used is obtained in the form of the solid hyposulphite, with a current efficiency of 60—70 per cent. The dry salt is unstable, about half of it being decomposed after three days' exposure to the air. T. E.

Behaviour of Borax towards Carbon Dioxide. LEO GRÜNHUT (*Zeit. physikal. Chem.*, 1904, 48, 569—576).—As shown by earlier workers, borax in aqueous solution is completely broken up into sodium metaborate and free boric acid. If carbon dioxide is passed through such a solution in the cold, the boric acid of the metaborate is also liberated and sodium hydrogen carbonate is produced. This has been established chiefly on the basis of conductivity experiments. If, after saturation with carbon dioxide, free boric acid is added in excess, a small quantity of metaborate is formed on account of mass action.

J. C. P.

Production of Isomorphous Mixtures of Lime and Lithia. PAUL LEBEAU (*Compt. rend.*, 1904, 138, 1602—1604. Compare this vol., ii, 561).—The double carbonate of lithium and calcium, obtained in the form of small, acicular crystals when a mixture of calcium carbonate (1 mol.) and lithium carbonate (2 mols.) is fused in an atmosphere of carbon dioxide and the product treated with a small quantity of water, is decomposed by excess of water, and when heated in a vacuum is dissociated, the dissociation pressure for any particular temperature being intermediate between those of the constituent salts. The product of complete dissociation is an isomorphous mixture of lime and lithia in the form of regular octahedral crystals, the composition of which varies with the temperature and duration of heating, as is represented in the following table :

| Composition of original mixture. | Temperature of heating. | Duration of heating. | Composition of final product. |
|----------------------------------|-------------------------|----------------------|-------------------------------|
| CaO : 2.46 Li ₂ O | 1200° | 7 hours | CaO : 0.24 Li ₂ O |
| CaO : 2.36 Li ₂ O | 1100 | 6 „ | CaO : 0.53 Li ₂ O |
| CaO : 2.35 Li ₂ O | 1350 | 4 „ | CaO : 0.16 Li ₂ O |
| CaO : 1.61 Li ₂ O | 1200 | 3 „ | CaO : 0.76 Li ₂ O |

The formation of these mixed crystals of lime and lithia indicates that the crystals of the latter belong to the cubic system.

M. A. W.

The Presence of Chlorine in Barium Sulphate, precipitated by Barium Chloride. GEORGE A. HULETT and L. H. DUSCHAK (*Zeit. anorg. Chem.*, 1904, 40, 196—217).—A method is described for estimating chlorine in barium sulphate, precipitated by barium chloride. The precipitate is dissolved in concentrated sulphuric acid and a current of purified air passed through the solution for two hours. In this manner, all the hydrogen chloride is expelled and estimated by being passed through an excess of *N*/100 silver nitrate solution. The amount of chlorine occluded in the barium sulphate precipitated by barium chloride may amount to as much as 1 per cent. and it is not possible to free the precipitate from it by washing. The amount of chlorine in the precipitate depends on the time the solution and precipitate have been agitated after precipitation ; the longer the stirring, the more does the percentage of chlorine in the precipitate diminish. It is also noted that when barium sulphate is first precipitated it is very finely divided, but the particles increase in size as stirring goes on. The amount of chlorine in the precipitate does not depend on the surface of the latter. No proportionality was found between the concentration of the barium chloride solution and the amount of chlorine in the precipitate. When the precipitation by barium chloride was conducted with solutions containing varying amounts of hydrochloric acid, the amount of chlorine in the precipitate increased with the concentration of the hydrochloric acid, the concentration of the barium chloride being kept constant, but the increase observed was not proportional to the concentration of the hydrochloric acid.

The precipitate of barium sulphate (containing chlorine) undergoes no diminution in weight when dried below 300° ; a diminution occurs, however, when the temperature exceeds 325° , and proceeds until the temperature reaches 600° , when no further loss is observed. When the precipitate is heated in an ignition tube between 300° and red heat, it parts with water and hydrochloric acid, but all the chlorine in the precipitate cannot be removed in this manner. Even when the barium sulphate is precipitated from neutral or faintly alkaline solution, it still parts with water and hydrogen chloride when heated. The loss in weight of the precipitate at temperatures varying from 150° to 957° was determined. When the precipitate is heated at 700° , the residue contains only barium sulphate and barium chloride. Between 650° and 900° , the residue is neutral; from 900° onwards a perceptible amount of chlorine is lost and the residue becomes alkaline.

A. McK.

Distillation of Mixtures of Two Metals. HENRI MOISSAN and ALPHONS O'FARRELLEY (*Compt. rend.*, 1904, 138, 1659—1664).—By the use of the electric furnace (compare Abstr., 1893, ii, 507), binary mixtures of metals which do not form carbides at the temperature employed, such as copper, zinc, cadmium, lead, and tin, can be separated completely or partially by fractional distillation, the alloys behaving in this respect like the three well-known types of liquid mixtures. The more volatile metal is completely separated from alloys of copper and zinc or copper and cadmium after one or two minutes' heating. Alloys of copper and lead behave on distillation like a mixture of partially miscible liquids such as ether and water. Tin and lead alloys behave like a mixture of alcohol and water, the residue consisting of pure tin, whilst alloys of copper and tin behave like a mixture of formic acid and water, yielding an alloy of constant boiling point containing about 60 per cent. of tin.

M. A. W.

The Yellow and Red Varieties of Thallous Iodide, the Determination of the Normal Point of their Reciprocal Transformation. DÉSIRÉ GERNEZ (*Compt. rend.*, 1904, 138, 1695—1697).—The transition point of the two varieties of thallous iodide is 168° , and not 190° as stated by Hebbeling (*Annalen*, 1865, 134, 18); the new value was determined by very slowly raising the temperature of a tube containing a thin layer of the yellow iodide which was sown from time to time with a small crystal of the red variety; at temperatures above the transition point, the yellow becomes red, and if the mass is then very slowly cooled, the inverse change occurs at the transition point. The two varieties can, however, retain their individuality for a range of temperature from -192° to $+200^{\circ}$, the yellow variety becoming orange-coloured on heating at the higher temperature limit, and paler yellow on cooling to the lower limit, the red variety becoming a much deeper red on heating to near its fusion point, and a paler red on cooling in liquid air.

M. A. W.

Thallous Nitrate and Nitrite. U. THOMAS (*Compt. rend.*, 1904, 138, 1697—1699).—When thallous nitrate is heated in a platinum

tube, it melts without decomposition at 205°, decomposes slowly at 300°, and very rapidly at 450°, with the formation of nitrogen trioxide, thallium sesquioxide, and a small quantity of oxygen and nitrogen, due probably to the decomposition of a small quantity of the nitrate into nitrite and oxygen, and the subsequent decomposition of the unstable nitrite according to the equation $2\text{TlNO}_2 = \text{Tl}_2\text{O} + \text{N}_2 + 3\text{O}$. The thallium trioxide obtained by this reaction is in a crystalline form and has a sp. gr. 9.97; Lepière and Lachaud give 5.56 (compare Abstr., 1892, 568). A small quantity of the thallous nitrate sublimes unchanged.

M. A. W.

Aluminium-magnesium and Aluminium-antimony Alloys. HECTOR PÉCHEUX (*Compt. rend.*, 1904, 138, 1606—1607. Compare this vol., ii, 564).—The aluminium-magnesium alloys containing less than 65 per cent. of aluminium, described by Boudouard (compare Abstr., 1901, ii, 141, 512), were obtained by fusing the two metals in sealed tubes out of contact of air.

Aluminium-antimony Alloys.—Von Aubel has prepared an alloy SbAl, melting at 1080°, Guillet the alloys SbAl, SbAl₃, SbAl₄, and SbAl₁₀, and Gautier has examined the melting points of alloys of the two metals. The author has prepared the following new alloys melting between 730° and 760°: SbAl₃₀, sp. gr. 2.736 at 23°; SbAl₃₅, sp. gr. 2.700; SbAl₃₈, sp. gr. 2.662; SbAl₄₀, sp. gr. 2.598; which expand on solidifying, are slightly sonorous and brittle, and can be bent readily. They are stable in the air at the temperature of fusion, bluish-grey in colour, do not decompose water in the cold, but the alloy SbAl₃₀ decomposes water at 100°; they are attacked by concentrated hot sulphuric acid, by cold dilute sulphuric acid, by cold concentrated nitric or hydrochloric acid or aqua regia, and by cold concentrated potassium hydroxide solution.

M. A. W.

Indium. I. ALFRED THIEL (*Zeit. anorg. Chem.*, 1904, 40, 280—336. Compare this vol., ii, 177, 410).—In the historical introduction, reference is made to the work on indium of Reich and Richter, Böttger, Weselsky, Nilson and Pettersson, Renz, and more particularly of Winkler.

The crude material used was obtained partly from a by-product of lead manufacture in the Upper Harz, and partly as metal. The pure metal is best obtained by dissolving the crude metal in dilute nitric acid and submitting this solution to fractional electrolysis, full details of the separation of indium from other metals being quoted.

The conversion of indium into nitrate and then into oxide is not a satisfactory method for determining the atomic weight of indium. The experiments show that temperatures of from 800° to 850° are insufficient for the preparation of the pure oxide if considerable quantities of substance are dealt with.

The conversion of indium into its dichloride, trichloride, and triiodide are also unsatisfactory for atomic weight determinations.

The amount of chlorine in indium trichloride, purified by sublimation in the absence of air, was determined. The method was a practical one for determining the atomic weight of indium, the value

found as a mean of four experiments being 115.05 ± 0.02 ($O = 16$). For details as to the precautions taken, the original paper may be consulted. The tribromide and tri-iodide gave unsatisfactory results.

Indium crystallises in octahedra; it is a very soft metal. It melts at $155^\circ \pm 1^\circ$, and not at 176° , as quoted by Winkler. When indium is allowed to remain in contact with water in the presence of air for several hours, a perceptible amount of indium hydroxide is produced. Indium is not acted on by dry air at the ordinary temperature.

Indium hydroxide readily forms colloidal solutions when washed with ammonia or with dimethylamine. Indium oxide is volatile at temperatures above 1000° . When heated in a current of hydrogen sulphide, indium oxide is converted into the scarlet sulphide. The sulphide, In_2S_3 , was prepared by heating the ordinary sulphide in a current of hydrogen. It was obtained mixed with the ordinary sulphide.

Indium monochloride readily decomposes into indium and indium trichloride.

Indium oxychloride is obtained by passing a current of chlorine and oxygen over fused indium dichloride.

Indium monobromide is the first product of the action of bromine on heated indium; it was obtained as a red liquid, which solidified to a carmine-red mass. It is acted on by water to form indium and indium tribromide. Indium dibromide, prepared by the further action of bromine on indium until the heated mass became dark yellow, solidifies to an almost colourless mass; by the action of water, it is converted into the mono- and tri-bromides. When vaporised, it is converted into the monobromide and bromine. Indium fluoride, $\text{InF}_3 \cdot 3\text{H}_2\text{O}$, prepared by the action of dilute hydrofluoric acid on indium oxide, forms rhombic pyramids; when its aqueous solution is boiled, indium hydroxide separates.

The electrical conductivity of indium chloride at varying dilutions was measured, as was also the potential of indium towards indium chloride.

A. McK.

Cementation of Carbon Steels and of Special Steels. LÉON GUILLET (*Compt. rend.*, 1904, 138, 1600—1602. Compare Abstr., 1903, ii, 483).—Cementation experiments with a mixture of wood charcoal and 5 per cent. of potassium carbonate in an atmosphere of air or nitrogen show that the diminution in the rate of penetration is due to the volatility of the alkali salt, the same phenomenon not being observed when barium carbonate is used instead of potassium carbonate.

The presence of small quantities of elements other than carbon in steel plays an important part in the process of cementation, according as the second element is present in the form of a carbide or merely in solution; thus manganese, chromium, tungsten, or molybdenum increases the rate of cementation of steels, whilst nickel, titanium, silicon, aluminium, or tin retard the cementation or stop it altogether.

Steels in which the iron is in the γ -state and which contain a large proportion of nickel and manganese were found, after cementa-

tion at 1200° for 8 hours, to contain 1.35 per cent. of carbon in the superficial layer. After remaining at the ordinary temperature for 6 months, the percentage had fallen to 1.05, and at the end of 12 months to 0.85, showing that γ -iron dissolves carbon even at the ordinary temperature.

M. A. W.

A New Molybdenum Carbide. HENRI MOISSAN and KARL HOFFMANN (*Compt. rend.*, 1904, 138, 1558—1561. Compare Abstr., 1895, ii, 500).—When a mixture of fused molybdenum, carbon, and excess of aluminium is heated in an electric furnace, a new *molybdenum carbide*, MoC , is obtained in the form of a grey, crystalline powder having a sp. gr. 8.40 at 20° and a hardness of 7 to 8. The carbide is not attacked by hydrogen at a red heat, burns readily in fluorine, forming carbon tetrafluoride and molybdenum fluoride, is attacked at a red heat by chlorine, at a higher temperature by bromine, and is only superficially attacked at a still higher temperature by iodine; is readily attacked by a mixture of hydrogen chloride and bromine vapour, and oxidised by heating in air or oxygen, by projecting on to fused potassium chlorate or nitrate, or by the action of cold nitric acid. It does not decompose water even at 500 — 600° , is only slowly attacked by hydrochloric, hydrofluoric, or sulphuric acid, whilst it is unaltered by solutions of alkali hydroxides.

M. A. W.

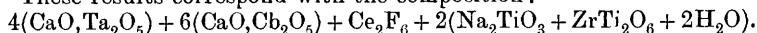
Mineralogical Chemistry.

Natron contained in the Urns of Maherpra (Thebes, Eighteenth Dynasty). LORTET and LOUIS HUGOUNENQ (*Compt. rend.*, 1904, 139, 115—118).—The contents of the urns is a greyish-yellow mixture containing 25 per cent. of resins and vegetable matter, 15 per cent. of sand and clay, and 60 per cent. of "soda," having the composition 27.13 per cent. of sodium chloride, 41.76 per cent. of sodium sulphate, $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$, and 31.09 per cent. of sodium sesquicarbonate, $\text{Na}_2\text{CO}_3, 2\text{NaHCO}_3, 3\text{H}_2\text{O}$ (compare Schweinfurth and Lewin, *Abstr.*, 1900, ii, 283). The resinous matter, extracted by alcohol, consists chiefly of myrrh with a little olibanum and bdellium. M. A. W.

Compositions of a Scandinavian Form of Pyrochlore and of the Minerals accompanying it. G. P. TSCHERNIK (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 712—746).—The pyrochlore described was obtained in the form of small, well-formed octahedral crystals having the sp. gr. 4.955; analysis gave:

| | | | | | | | |
|--------------------|----------------------------------|-----------------------------------|----------------------------------|---------------------------------|--------------------|--------------------|--------------------|
| CaO. | Ta ₂ O ₅ . | Clb ₂ O ₅ . | Ce ₂ O ₃ . | Y ₂ O ₃ . | ThO ₂ . | ZrO ₂ . | TiO ₂ . |
| 10.62 | 33.03 | 30.70 | 5.90 | 0.46 | traces | 4.65 | 9.11 |
| Na ₂ O. | MgO. | H ₂ O. | F. | Total. | O = 2F. | Total. | |
| 2.35 | traces | 1.37 | 2.17 | 100.36 | 0.91 | 99.45 | |

These results correspond with the composition :



Zircon was found with the above in badly-formed, brownish-yellow crystals, somewhat larger than those of the pyrochlor and having the sp. gr. 4.55. Analysis gave the numbers :

| SiO_2 . | ZrO_2 . | Fe_2O_3 . | CaO . | MgO . | H_2O . | Total. |
|------------------|------------------|---------------------------|----------------|----------------|------------------------|--------|
| 32.44 | 65.76 | 0.42 | 0.09 | traces | 0.46 | 99.17 |

corresponding with the formula $\text{SiO}_2, \text{ZrO}_2$.

Titanic iron ore, mixed with the two preceding minerals, has the sp. gr. 4.755 and the composition :

| TiO_2 . | FeO . | MnO . | CaO . | MgO . | Total. |
|------------------|----------------|----------------|----------------|----------------|--------|
| 52.50 | 44.32 | 1.36 | 0.06 | 0.79 | 99.03 |

corresponding with the formula TiO_2, FeO .

T. H. P.

Analysis of Kunzite. R. O. E. DAVIS (*Amer. J. Sci.*, 1904, [iv], 18, 29. Compare this vol., ii, 53).—Analysis of a deep lilac-coloured crystal gave the following results :

| SiO_2 . | Al_2O_3 . | NiO . | MnO . | ZnO . | CaO . | K_2O . | Na_2O . | Li_2O . | Loss on ignition. | Total. |
|------------------|---------------------------|----------------|----------------|----------------|----------------|------------------------|-------------------------|-------------------------|----------------------|--------|
| 64.65 | 27.30 | 0.06 | 0.11 | 0.44 | 0.80 | 0.06 | 0.30 | 6.88 | 0.15 | 100.15 |

There is an absence of Mg, Cr, V, Ti, Fe, Sr, Ba, Th, Zr, Ce, Y, P. The mineral loses its pink colour on ignition.

L. J. S.

New Theory of Uralitisation. LOUIS DUPARC and TH. HORNING (*Compt. rend.*, 1904, 139, 223—225).—A series of magnetite-pyroxene-amphibole-labradorite rocks from Cérébriansky, in the northern Urals, show all stages in the passage from pyroxene to green amphibole, and are especially suitable for the study of the phenomenon of uralitisation. Analyses of the pyroxene and amphibole isolated from these rocks gave the results under I and II respectively, which dispose of the idea that the process of uralitisation is one of molecular transformation. The fact that the rocks are perfectly fresh also disposes of the theory of hydrochemical alteration. It is suggested that after the pyroxene crystallised out it was acted on by the residual magma and transformed in patches into amphibole.

| SiO_2 . | Al_2O_3 . | Fe_2O_3 . | FeO . | MnO . | CaO . | MgO . | K_2O . | Na_2O . | Loss on ignition. | Total. | Sp.gr. |
|------------------|---------------------------|---------------------------|----------------|----------------|----------------|----------------|------------------------|-------------------------|----------------------|--------|--------|
| I. 50.91 | 2.64 | — | 10.07 | trace | 23.33 | 13.30 | nil | nil | nil | 100.25 | 3.358 |
| II. 43.34 | 12.60 | 10.44 | 7.92 | trace | 13.06 | 12.60 | 0.02 | 1.90 | 0.22 | 102.10 | 3.213 |

L. J. S.

Physiological Chemistry.

Experiments made on Monte Rosa on the Respiration of Pure Oxygen and of Oxygen mixed with Carbon Dioxide. A. Mosso (*Atti Real. Accad. Lincei*, 1904, [v], 13, i, 670—680).—In Turin, the breathing of pure oxygen by a man produced no change in the respiration or pulse, but on Monte Rosa it altered the frequency of pulsation from 54 to 50 per 30 seconds and that of respiration from 22 to 20 per minute. On Monte Rosa, respiration of a mixture of 31 per cent. (? by volume) of carbon dioxide and 69 of oxygen produced a change in the frequency of the pulse from 60 to 50 per half minute and in that of respiration from 22 to 30 per minute; the patient experienced such a strong stimulus to breathe that it was impossible to hold the breath, and he felt that the thorax could be expanded better. In Turin, a similar mixture of carbon dioxide and oxygen was found to increase the frequency of pulsation from 30 to 36 per half minute, and that of respiration from 20 to 32 per minute; it quickly produced inconvenience, irritation of the throat, and slight dizziness, accompanied by an acid taste. These experiments were repeated on another man and on a dog, the results being similar to those just described.

T. H. P.

Further Observations on the Densimetric Method. AUGUSTUS D. WALLER and B. J. COLLINGWOOD (*Proc. physiol. Soc.*, 1904, xxxvii—xlili; *J. Physiol.*, 31).—It is possible to determine the respiratory quotient (R) without a volumetric measurement of oxygen absorption by the formula $R = 0.34p/1.68p - m$, where p represents the percentage of carbon dioxide determined volumetrically, and m is the densimetric increment per 250 c.c. in milligrams. The way in which this formula is obtained is explained on simple mathematical grounds, and the fact that approximately accurate results are obtained is adduced as further evidence that the densimetric estimation of heavier substances like chloroform and ether vapour is trustworthy.

W. D. H.

Density of Expired Air and Respiratory Quotient. W. LEGGE SYMES (*Proc. physiol. Soc.*, 1904, lii—lv; *J. Physiol.*, 31).—Further mathematical treatment of the same problem. W. D. H.

Specific Gravity of Blood. O. INCHLEY (*Proc. physiol. Soc.*, 1904, xxxlii—xxxv; *J. Physiol.*, 31).—A number of standard bottles containing a mixture of chloroform and light petroleum and beads of known specific gravity. Drops of blood are introduced by means of a special pipette, which is described and figured.

W. D. H.

Carbon Dioxide of Venous Blood and Alveolar Air in Cases of Diabetes. A. P. BEDDARD, MARCUS S. PEMBREY, and E. I. SPRIGGS (*Proc. physiol. Soc.*, 1904, xlii—xli; *J. Physiol.*, 31).—A series of analyses shows that there is a relation between the alkalinity and amount

of carbon dioxide in venous blood, the two rising and falling together without being actually parallel. In the hyperpnœa of diabetic coma, there is a great reduction in the amount of carbon dioxide in the alveolar air, and an increase in the quantity of oxygen, but in diabetes without coma the former gas may be within normal limits. The low percentage of carbon dioxide in the alveolar air can be produced in a normal man at rest, and contrasts markedly with the condition of dyspnœa in heart disease, pernicious anæmia, and with the hyperpnœa of healthy men during exercise. It is probable that the respiratory centre is stimulated by substances other than carbon dioxide, and that in diabetic coma the hyperpnœa reduces the volume of carbon dioxide in the venous blood, for the pressure of alveolar carbon dioxide falls to 2.2 per cent. of an atmosphere. By treatment of such patients with injections of sodium hydrogen carbonate, the typical great ventilation of the chest usually disappears.

The present observations do not support the view that the low proportion of carbon dioxide in the venous blood in diabetic coma is directly dependent on the reduced alkalinity and a reduced carrying power of the blood for that gas. They suggest that the hyperpnœa is a cause, and not the effect, of the reduction of the carbon dioxide in the blood. Experiments still in progress indicate that there is also a diminished production of carbon dioxide.

W. D. H.

Albumoses in Blood. EMIL ABDERHALDEN and CARL OPPENHEIMER (*Zeit. physiol. Chem.*, 1904, 42, 155—156).—Investigation of the plasma and serum of various animals led to the result that albumoses are usually absent from these fluids, or, if occasional traces occur, the amount is negligible so far as physiological importance is concerned.

W. D. H.

Choline in Blood and Cerebrospinal Fluid. RICHARD W. ALLEN (*Proc. physiol. Soc.*, 1904, lvi—lviii; *J. Physiol.*, 31).—A modification of the iodine test for choline is proposed, which avoids any risk of confusing that substance with alkaline chlorides. The results obtained confirm those previously given by Mott and Halliburton, who mainly used the platinic chloride test. Provided a nervous lesion is sufficiently extensive or acute, choline can be detected in the circulating fluids of the body. Cases of epilepsy gave negative results. Injection of choline into the brain substance directly is the only way in which it produces convulsions, but these are attributed, not to the drug, but rather to cerebellar irritation and increase of pressure. After repeated injections into the brain of the rabbit, there is a peculiar diffuse degeneration produced in some of the fibres of the spinal cord, especially in the dorsal region, great muscular weakness, and a peculiar change in the joints of the forelegs. No obvious effect has been produced in rats.

W. D. H.

The Choline Test in Cerebrospinal Fluid. G. MANSFELD (*Zeit. physiol. Chem.*, 1904, 42, 157—164).—A criticism of Donath's work

(this vol., ii, 63). The crystals he described are stated to consist, not of choline platinichloride, but of ammonium platinichloride.

W. D. H.

Embryonic Ferments. MARCUS HARTOG (*Proc. physiol. Soc.*, 1904, xlvii; *J. Physiol.*, 31).—An examination of the segmenting eggs of the frog shows the presence of a peptic ferment only active in acid liquids. A similar ferment was detected in the extra-vascular blastoderm of the chick of 2 to 4 days' incubation, with indication also of an inverting ferment. These ferments are very fugacious, disappearing from material treated with alcohol in the course of a few weeks, and from material in thymolised physiological salt solution in three weeks in the dark.

W. D. H.

Solutions in which Sea Urchins' Eggs Develop. JACQUES LOEB (*Pflüger's Archiv*, 1904, 103, 503—509).—A further contribution to the subject on the lines of the author's previous work.

W. D. H.

Influence of Fasting and Feeding on Metabolism. MARCUS S. PEMBREY and E. I. SPRIGGS (*J. Physiol.*, 1904, 31, 320—345).—The percentage composition of well-fed rats is 17 to 22 parts proteid, 4 to 11 fats, and 60 to 70 water. After fasting for three days, a rat contained 2·68 per cent. of fat, which is so little less than in some normal animals that deductions are difficult. During fasting, the respiratory exchange quickly reaches a minimum, and then remains constant; the respiratory quotient falls to 0·75 or even 0·63. If the animal were feeding on its own fat, these numbers are too low; possibly some fat is converted into glycogen and sugar. An animal which had by fasting reached the minimal respiratory exchange is taken as the unit in feeding experiments; the effect of food rich in carbohydrates is well marked within an hour, and increases for 2 or 3 hours; the rise in the output of carbon dioxide varied from 14 to 97 per cent. of the minimal discharge during hunger. The increase in the absorption of oxygen was 9 to 35 per cent., but in three cases it fell below the minimum. This may be due to lessened muscular activity after food; or by the fact that carbohydrates yield more heat than do fat and proteid, when the consumption of oxygen is equal; thus the animal can satisfy its needs of energy by a smaller absorption of oxygen. The respiratory quotient after a meal rich in carbohydrates may rise to 1·17, and remain at 1·14 for 20 hours. This is due to increase in carbon dioxide discharged, not to decrease in absorption of oxygen, and is explained by the conversion of carbohydrates into fats, accompanied by an elimination of carbon dioxide. There is a general increase in the body metabolism. Calculations based on the theory that the quotients above unity are due to formation of fat give 0·59, 1·13, and 1·09 grams as the amount of fat deposited during the first three days of feeding. Calculations based on the data for the total respiratory and nitrogenous exchange give 2·30 and 2·65 grams as the daily amounts of fat that underwent combustion in the fasting rats. The heat produced during 24 hours is calculated to be 26,585

and 23,668 cal. for the fasting rats, and 32,812 and 29,460 cal. for the same animals after feeding.

A fast preceding a meal acts as a marked stimulus to the assimilation of food. Rats during fasting lose 5 to 8 per cent. of their weight in 24 hours, and during the first day of feeding gain a similar weight when allowance is made for the food in the alimentary canal.

The respiratory quotient is probably the resultant of quotients above and below the theoretical values for the combustion of proteids, carbohydrates, and fats.

W. D. H.

Addition of Sodium Citrate to Cows' Milk in Infant Feeding. F. I. POYNTON (*Lancet*, 1904, ii, 433—436).—In cases where it is necessary to use cows' milk in infant feeding, it is recommended that from 1 to 3 grains of sodium citrate be added per ounce. By causing partial decalcification, the formation of the usual massive curd is prevented. The added drug is harmless, and good results in all cases so treated are recorded.

W. D. H.

Condition of Starch in Stale Bread. E. ROUX (*Compt. rend.*, 1894, 138, 1356—1358).—The starchy matter of stale bread seems to possess the same food value as in fresh bread.

In the case of flour, the soluble matter diminishes, whilst amylo-cellulose increases. The change is not influenced by addition of the same amount of sodium chloride as is employed in bread making.

N. H. J. M.

Alanine-feeding in Dogs without a Pancreas. GUSTAV EMBDEN and H. SALOMON (*Beitr. chem. Physiol. Path.*, 1904, 5, 507—509).—In a dog without a pancreas, and taking 200 grams of meat free from fat daily, the amount of sugar excreted per diem remained constant between 16 and 17 grams. One day, it received in addition 14 grams of alanine by the mouth and 20 grams subcutaneously; the sugar excreted rose to 29.3 grams and next day fell to 19. In another dog, the sugar excreted was reduced by absence of food to 2—4 grams daily; on the days when alanine was given, it rose to 18—19 grams. Whether the alanine is directly converted into sugar is not discussed.

W. D. H.

Auto-digestion of Nucleo-proteids. WALTER JONES (*Zeit. physiol. Chem.*, 1904, 42, 35—54).—In auto-digestion of the thymus, xanthine, a small amount of hypoxanthine, and uracil are formed, but not guanine, adenine, or thymine, although these are produced by the action of mineral acids on thymus-nucleic acid. In auto-digestion of the suprarenal body, xanthine and a small amount of hypoxanthine are found, whilst by hydrolysis of the nucleo-proteid of the gland with boiling acids, guanine and adenine are formed. No noteworthy amount of leucine is formed. In auto-digestion of the spleen, guanine is formed as abundantly as in hydrolysis by acid of its nucleic acid; hypoxanthine is also formed on autolysis, and instead of adenine and uracil, as expected, thymine and cytosine are formed as on hydrolysis. The cause of these differences is discussed.

W. D. H.

Protective Value of Proteids and their Decomposition Products on Trypsin. HORACE M. VERNON (*J. Physiol.*, 1904, 31, 346—358).—The protective value of various substances on trypsin was estimated by keeping pancreatic extract with 0·4 per cent. sodium carbonate solution and a known percentage of the substance for 1 hour at 38°, and determining the amount of trypsin thus destroyed. The protective value depends principally on the power the substance possesses of neutralising the alkali, and so rendering it incapable of reacting on the ferment. Most proteids have the same protective value, 45 per cent. of the trypsin being destroyed in the presence of 0·4 per cent. of proteid, 27 per cent. in presence of 1 per cent. proteid, 12 per cent. in presence of 2 per cent. proteid, and 7 per cent. in presence of 4 per cent. proteid. When no proteid was present, 56 per cent. was destroyed. Hydrated proteids have a slightly greater protective value than native proteids, and the products of proteid hydrolysis a slightly greater one still. Aspartic acid and glycine have a somewhat greater value than proteids, leucine and hippuric acid about the same value, bile acids much less, whilst urea, creatine, and the sugars have none at all. If the acid radicles in various substances are neutralised previously, they lose their protective value.

In certain cases there is a combination between ferment, molecule, and proteid. Thus egg-albumin has a marked anti-tryptic action, the digestive power of the trypsin being reduced to 29 and 2·9 per cent. of its normal value in the presence of 0·05 and 1 per cent. of the proteid respectively. Also, a mixture of Witte's peptone with sodium carbonate sufficient for its complete neutralisation exerts a considerable protective action on the ferment. W. D. H.

Alimentary Origin of Arsenic in Man. ARMAND GAUTIER and P. CLAUSMANN (*Compt. rend.*, 1904, 139, 101—108).—The arsenic stated to be found in animal tissues is regarded as indispensable, not accidental. Accordingly various foods were examined in order to determine whence is derived this element, which is continually being got rid of by desquamation of the epidermis and by the excretions; forty different kinds of foods, animal, vegetable, wines, beer, water, salt, &c., were analysed, and arsenic was found in all, with two exceptions, beans and cabbages. It is specially abundant in the flesh of fish and crustacea. In the daily diet, it is calculated there are 21 thousands of a milligram, and in the year 7·6 mg. are taken, which are regarded as sufficient for the needs of the body. W. D. H.

Arsenic in Nutriment. V. BORDAS (*Compt. rend.*, 1904, 139, 234—236).—The harmful effect of arsenic, for instance, in producing neuritis when taken in beer has led the author to analyse various preparations of glycerol, glycerophosphates, phosphoglycerates, chicory, and malt. The amount of arsenic found in many cases is sufficiently great to produce alarm, especially if the products are consumed or used in the preparation of the food consumed by young children for a prolonged period. W. D. H.

Localisation of Iodine in the African Turtle. MAURICE DOYON and CHENU (*Compt. rend.*, 1904, 139, 157—158).—The amount of iodine in the thyroid, parathyroids, carapace, and eggs of the turtle are given. The parathyroids contain none, the other parts mentioned a few milligrams.

W. D. H.

Oxidation in Animal Tissues. III. AN. K. MEDVEDEFF (*Pflüger's Archiv*, 1904, 103, 403—428).—An investigation of the oxidative action of liver extracts on salicylaldehyde. This is lessened or abolished by treatment with trypsin, but not with chloroform. The ferment is weakened by the accumulation of the product of its action (salicylic acid). Mathematical formulæ relating to the velocity of the reaction in varying circumstances are given. The active substance or ferment is doubtless of proteid nature, and in some way acts as a hydrogen consumer of the substance oxidised.

W. D. H.

Reaction of Brain. FRANZ MÜLLER and A. OTT (*Pflüger's Archiv*, 1904, 103, 493—502).—Attempts to resuscitate the brain of animals by oxygenated salt solutions, as in the work of Locke, Kuliabko, and others on the heart, failed. When the supply of blood to the brain ceases, the grey cortex rapidly undergoes changes that cause it to react acid to litmus.

W. D. H.

Nature of Chemical and Electrical Stimulation. ALBERT P. MATHEWS (*Amer. J. Physiol.*, 1904, 11, 455—496).—From experiments on frogs' nerves, the conclusion is drawn that the action of a chemical reagent is dependent on the electrical state and stability of the ion, and is independent of chemical composition, except as the chemical composition may influence its velocity and weight. Chemical stimulation is thus electrical and dependent on the electrical charges of the ions. Whether any salt stimulates or depresses depends on the relative efficiency of its anion and cation. If the anion predominates as in hydrates, the salt stimulates; if the cation, it depresses. In other words, the ions are freely moving electrodes; the chemical composition of an electrode is of little importance compared with its electrical condition.

W. D. H.

Action of Oxygen on Corneal Endothelium. G. BULLOT (*J. Physiol.*, 1904, 31, 359—364).—If the eyeball of a rabbit has its corneal epithelium scraped off and is placed in moist air at 35° for 15 hours, the endothelium that covers the posterior surface of the cornea is still alive, as determined by its resistance to staining reagents. If, instead of air, a mixture of 1 part of air to 14 parts of hydrogen is employed, the endothelium is dead; this is regarded as equivalent to rarefying the air to 1/15. The same result is obtained with pure hydrogen. If the rarefaction is only 1/7 or 1/10, the endothelium remains alive in the centre, but is dead at the periphery; this was formerly supposed to be due to toxic material produced in the surrounding ciliary body. In pure oxygen up to 2.2 atmospheres the endothelium remains alive; if the pressure is increased to 3 to 4 atmospheres, it is killed; if the

pressure is 2.4 atmospheres, the central region only is killed. The explanation previously advanced of a toxic substance is therefore abandoned, and the difference in behaviour to varying pressures must be due to physiological differences in the cells of the two regions.

W. D. H.

Lipase of the Liver. RUDOLF MAGNUS (*Zeit. physiol. Chem.*, 1904, 42, 149—154).—The ester-splitting ferment or lipase of the liver, as in the case of certain other enzymes, depends for its action on the presence of two substances. These are both contained in liver extracts, and can be separated by dialysis; one, the ferment, is not dialysable and is destroyed by heat; the other, called the 'co-ferment,' is dialysable and is not destroyed by boiling; its chemical nature is not known. Neither component by itself is effective.

W. D. H.

Chemical Composition of Fish. H. LICHTENFELT (*Pflüger's Archiv*, 1904, 103, 353—402).—The composition of the muscles of fish periodically changes with age, nutrition, and reproduction. Hunger increases the amount of water and diminishes the solids; the richer in fat the muscles were before, the more marked is this diminution; the amount of proteid goes down too, not only in the salmon but in other fishes also; the loss falls chiefly on the insoluble proteids. The soluble proteid, especially if work is done, may increase.

W. D. H.

The so-called Chlorophyll of Silk. JULES VILLARD (*Compt. rend.*, 1904, 139, 165—166).—The green pigment of certain silk is not chlorophyll as alleged by Levrat and Conte. This conclusion agrees with that of Dubois.

W. D. H.

Destruction of Adrenaline in the Living Animal. OTTO WEISS and J. HARRIS (*Pflüger's Archiv*, 1904, 103, 510—514).—The return of the blood pressure to the normal after an injection of adrenaline is not due to the rapid disappearance of the drug from the circulation, for if the blood is collected and a portion injected into another animal the usual rise of pressure is seen in that animal. The return of the pressure to normal is not attributed to nervous mechanism, but is probably due either to fatigue of the muscles of the vessels, or to the circumstance that they become accustomed to the stimulus.

W. D. H.

Purine Bases of Herring Brine. S. ISAAC (*Beitr. chem. Physiol. Path.*, 1904, 5, 500—506).—Guanine, adenine, hypoxanthine, and probably xanthine were identified. The most abundant bases were guanine and hypoxanthine. They are believed to originate mainly from the nuclein substances in the testis.

W. D. H.

Phosphoric Acid in Cerebrospinal Fluid in Nervous Diseases. JULIUS DONATH (*Zeit. physiol. Chem.*, 1904, 42, 141—148).—Choline, a product of the breaking down of lecithin, is found in the cerebrospinal fluid in cases where the disintegration of nervous tissue is sufficient.

In the present paper, the question is asked whether in such cases the amount of phosphoric acid (also a product of lecithin decomposition) is increased also. In a case of tumour of the brain and in several cases of locomotor ataxy and progressive paralysis, the answer is in the affirmative; here also the amount of proteid in the fluid is increased. In cases of what are called functional diseases (epilepsy, melancholia, neurasthenia, hysteria), there is no such increase of either phosphoric acid or proteid.

W. D. H.

Bacteriology of Empyema. W. J. S. BYTHELL (*J. Pathol. Bacteriol.*, 1904, 9, 365—399).—In a paper dealing with the pathology of empyema in children, the results of previous observers are confirmed that the two most important bacteria are the *pneumococcus* (especially) and the *streptococcus*. The latter organism produces milder symptoms. Tuberculosis is often present also. Infection of the pleura usually comes from a pulmonary lesion.

W. D. H.

Fate of Certain Aromatic Acids in Alcaptonuria. OTTO NEUBAUER and W. FALTA (*Zeit. physiol. Chem.*, 1904, 42, 81—101).—In alcaptonuria, tyrosine and phenylalanine are not completely burnt, as in normal people, but are excreted as diphenolic acids (homogentisic and uroleucic acids). In order to determine whether a similar fate attends other aromatic acids, these were given by the mouth to a patient suffering from the condition, and an increase, if any, in the homogentisic acid excreted noted. Non-hydroxylic aromatic acids (phenylacetic, phenylpropionic, phenylacrylic) do not pass out as homogentisic acid; the same is true for monophenolic acids (*p*-coumaric, *o*-coumaric) and coumarin, and for diphenolic acids. It is only the aromatic and hydroxy-acids (phenyl- α -lactic, phenyl- β -lactic, phenylglyceric, &c.) which are excreted as homogentisic acid. These are regarded as intermediate products in the metabolic destruction of proteid. Theoretical deductions on the way in which aromatic substances are split off from proteid molecule are given.

W. D. H.

Hæmatoporphyrinuria not due to Sulphonal. ARCHIBALD E. GARROD (*Trans. Path. Soc. London*, 1904, 55, 142—151).—Hæmatoporphyrinuria occasionally but rarely occurs in cases in which the influence of sulphonal or trional can be excluded; details and references to such cases are given. When not due to these drugs it is not specially met with in females, and has no particularly unfavourable prognostic significance. It may persist for many years, or recur intermittently. There is no evidence of serious implication of the liver in such cases.

W. D. H.

Lethal Action of Acids and Bases on *Paramœcium Aurelia*. J. O. WAKELIN BARRATT (*Proc. Roy. Soc.*, 1904, 74, 100—104).—The minimal lethal doses of various acids and alkalis on known weights of *Paramœcium* are determined and the results given in tables. The considerable difference in ionic concentration both of acids and of bases for a nearly equal toxic effect shows that such effect is not hydrolytic in character, for in such a case the concentration of H^+ or

OH⁻ ions would be constant in each series. The relation between periodic grouping and lethal character exhibited by strong alkalis supports the view that the latter is dependent on a chemical reaction not hydrolytic in character.

W. D. H.

Action of Poisons on Kidney and Spleen. GEORGE LYON (*J. Pathol. Bacteriol.*, 1904, 9, 400—455).—Diphtheria toxin, mercuric chloride, and cantharidin produce acute inflammatory conditions of the kidney in animals, but the changes are not analogous to those seen in man, the most marked difference being that after the administration of the poison ceases the kidney returns to the normal condition, and the inflammation is not followed by chronic or subacute changes resulting in fibrosis. The bulk of the paper deals with the histological changes described. Destruction of red corpuscles by phagocytes in the splenic pulp is a marked feature in all cases.

W. D. H.

Action of Krait Venom. R. H. ELLIOTT and W. C. SILLAR (*Proc. Roy. Soc.*, 1904, 74, 108—109).—The symptoms produced by the venom of the common krait (*Bungarus ceruleus*) are similar to those of cobra poisoning, although there are great differences in relative degree. There was no evidence of hæmolysis or ante-mortem clotting in the blood. Minimal lethal doses for various animals are given. Calmette's serum is no protection.

W. D. H.

Action of Sea Snake Venoms. I. THOMAS R. FRASER and R. H. ELLIOTT (*Proc. Roy. Soc.*, 1904, 74, 104—108).—The minimal lethal doses of the venoms of *Enhydrina valakadien* and *E. curtus* are given for various animals and compared with that of cobra venom. The *E. valakadien* is the most poisonous of the three. In the main, the symptoms are alike throughout, but dyspnœa is more urgent, and cardiac effects less so with the sea snakes as compared with the cobra. Calmette serum only feebly antagonises the sea snake venom.

W. D. H.

Action of Scorpion Venom. W. H. WILSON (*Proc. physiol. Soc.*, 1904, xlviii—xlix; *J. Physiol.*, 31).—The main symptoms, observed chiefly in experiments on guinea-pigs, are hypersecretion, convulsions followed by prolonged muscular spasms, and death from asphyxia. The body temperature is usually slightly raised. In dogs there is a good rise of arterial pressure, followed by a gradual fall and slowing of the heart. The coagulability of the blood is not altered; there is early onset of *rigor mortis*. The effect on muscle is a direct one; nerve trunks are not affected, and there is no excessive reflex excitability; the spasms in a frog are not removed by the destruction of the spinal cord. The simple muscle nerve resembles in many ways that produced by veratrine, that is, a condition in which the phenomena of fatigue are exaggerated. Cardiac and plain muscle react in a similar way.

W. D. H.

Immunity of Certain Desert Animals to Scorpion Venom. W. H. WILSON (*Proc. physiol. Soc.*, 1904, l—lii; *J. Physiol.*, 31).—The

animals inhabiting the Egyptian desert must frequently come into contact with scorpions. It therefore seemed probable that they would possess sufficient immunity to protect them from the fatal effect of a scorpion's sting. The examination of several kinds of desert animal (jerboa, gerbillus, &c.) shows that this is actually the case. These animals have a resistance nearly 300 times as great as that of the guinea-pig. The blood of these animals does not possess the power of destroying the active principle of the venom *in vitro*, and their isolated muscles are just as readily affected as those of rat or guinea-pig.

W. D. H.

Action of Potassium Salts on the Heart and Vessels of Mammals. LUDWIG BRAUN (*Pflüger's Archiv*, 1904, 103, 476—492).—Intravenous injection of potassium salts produces an effect both on heart and blood vessels. Quite small doses (0.005 to 0.01 gram) in a rabbit produce a rise of blood pressure and an increase in the heart rate. Larger doses (0.01 to 0.2 gram) produce a fall of blood pressure followed by a rise due to vaso-constriction. Lethal doses kill by stopping the heart, as Blake pointed out in 1839. With large doses which are not fatal, there is only a fall of blood pressure of cardiac origin; on the recovery, the "vagus pulse" is well seen. The heart, before it ceases to beat, exhibits fibrillary twitchings. Previous atropinisation makes no difference to the result. Vaso-dilatation was never seen. The therapeutic use of potassium as a heart stimulant is contra-indicated.

W. D. H.

Action of Amyleine Hydrochloride on Cilia. L. LAUNOY (*Compt. rend.*, 1904, 139, 162—165).—The local application of this drug to the pharynx of the frog produces a temporary tonic effect on, followed by an adynamic condition of, the cilia.

W. D. H.

Behaviour of $\alpha\beta$ -Diaminopropionic Acid in the Body. PAUL MAYER (*Zeit. physiol. Chem.*, 1904, 42, 59—64).—Subcutaneous injection of the hydrochloride of $\alpha\beta$ -diaminopropionic acid into rabbits produces temporary dyspnoea; the free acid is very poisonous. After one dose of 5 to 10 grams, neither the unaltered acid nor glyceric acid could be found in the urine, but after more prolonged dosage a small quantity of glyceric acid was found, showing that the diamino-acid had been deprived of both its amino-groups.

W. D. H.

Action of Sodium Sulphite, Aldehyde Sodium Hydrogen Sulphite, Acetone Sodium Hydrogen Sulphite, and Other Substances on Toads. FR. FRANZ (*Chem. Centr.*, 1904, ii, 141—142; from *Arch. Kais. Ges.-A.*, 21, 304—311).—Experiments on toads have shown that solutions of normal sodium sulphite, aldehyde sodium hydrogen sulphite, and acetone sodium hydrogen sulphite of concentrations equivalent respectively to 0.224, 0.672—0.896, and 0.112 per cent. of sulphur dioxide caused death within the same time. Solutions which were fatal to toads also caused the death of other animals within 42 hours. Solutions containing less than 0.112, 0.448—0.672, and 0.0224 per cent. respectively of sulphur dioxide in the form of

sodium sulphite and the compounds of aldehyde and acetone appeared to have no effect. Experiments have also been made with sodium chloride, sodium nitrate, sodium sulphate, sodium carbonate and sodium borate, sodium bromide, sodium iodide, sodium fluoride, and boric acid. A 1/100 normal solution of sodium fluoride was found to kill toads within 8—44 hours, whilst a 1 per cent. solution of boric acid or a 1.01 per cent. solution of borax was fatal in $3\frac{1}{4}$ —16 hours.

E. W. W.

Comparative Tests of the Pharmacological Action of Sulphurous Acid contained in Organic Compounds and that Contained in Normal Sodium Sulphite. EUGEN ROST and FR. FRANZ (*Chem. Centr.*, 1904, ii, 142; from *Arb. Kais. Ges.-A.*, 21, 312—371. Compare Kerp, this vol., i, 713).

Pharmacological Examination of Corydalis Alkaloids. FRIEDRICH PETERS (*Chem. Centr.*, 1904, ii, 145; from *Arch. exp. Path. Pharm.*, 51, 130—174).—Experiments on frogs, guinea-pigs, rabbits, cats, and dogs have shown that the corydalis alkaloids may be divided, according to their physiological action, into three classes, which are identical with those suggested by their chemical behaviour (compare Gadamer, *Abstr.*, 1902, i, 306, 391). Corytuberine differs physiologically, as well as chemically, from the other alkaloids; it does not directly attack the heart, and has no narcotic effect on frogs. The alkaloids of the corydaline group resemble those of the morphine group, and cause paralysis of the spinal marrow. The corycavine alkaloids excite the motor centres. The bulbocapnine group are analogous to the codeine alkaloids and increase reflex excitability in the case of frogs.

E. W. W.

Effect of Suprarenal Extract on the Frog's Pupil. S. J. MELTZER and CLARA MELTZER AUER (*Amer. J. Physiol.*, 1904, 11, 449—454).—In mammals, adrenaline produces no effect on the pupil, whether given subcutaneously or locally applied; dilatation does, however, occur after intravenous injection if the superior cervical ganglion is previously removed.

In frogs, the case is different. Extreme and prolonged dilatation is the result of either method of administration, even after the eye has been removed from the body. This reaction may be used as a test for adrenaline.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Destruction of Bacteria [in Water] by Aëration and by Hydrogen Peroxide. KÜSTER (*Arch. Hygiene*, 1904, 50, 364—387).
—The number of germs in water is considerably diminished by

aération when the water is at the same time cooled by means of ice. Cooling alone had a slight effect.

Hydrogen peroxide was found to have considerable value as a disinfectant, and its employment for purifying small quantities of water is recommended.
N. H. J. M.

Absence of *Bacillus Coli* in Unpolluted Water. A. C. HOUSTON (*J. Pathol. Bacteriol.*, 1904, 9, 456—471).—*Bacillus coli* is present in large quantities in sewage, and there is a broad parallelism between the number of the bacilli in sewage-polluted waters and the degree of contamination with sewage. In order to make the importance of the bacilli more evident, it is necessary to show further that the *B. coli* is absent from relatively large quantities of unpolluted sea water and the water of tidal rivers; this is what the bulk of the present paper is concerned in proving is the case.
W. D. H.

Detection of *Bacillus Enteritidis Sporogenes* in Water. R. TANNER HEWLETT (*Trans. Path. Soc. London*, 1904, 55, 123—126).—A modification in the manner of carrying out the milk test for this sewage microbe is suggested.
W. D. H.

Respiration-enzymes of Moulds. S. KOSTYTSCHEFF (*Chem. Centr.*, 1904, ii, 48—49; from *Ber. Deutsch. Bot. Ges.*, 22, 207—215).—The following conclusions have been derived from the results of experiments. (1) The absorption of oxygen and the liberation of carbon dioxide by moulds in the process of respiration is at least partly due to the action of specific enzymes. (2) The formation of carbon dioxide when oxygen is excluded is effected by means of an enzyme which is not identical with Buchner's zymase. (3) Stoklasa and Czerny's theory of the formation of zymase by aerobic organisms is not quite correct (*Abstr.*, 1903, ii, 320). (4) Although the enzyme concerned in the process of "anaerobic" respiration also occurs in organisms which have lived under conditions in which they had access to oxygen, it cannot be assumed that anaerobic respiration is the initial stage of normal respiration, since (5) by drying the acetone preparation in absence of oxygen at 100° it may be rendered inactive, whilst if oxygen is not excluded the activity is not destroyed.
E. W. W.

Relation of *Staphylococcus Pyogenes Aureus* to Rheumatic Fever. F. J. POYNTON and W. V. SHAW (*Trans. Path. Soc. London*, 1904, 55, 126—140).—This micro-organism is not the cause of rheumatic fever either in simple or mixed infection. Rheumatic fever is not an attenuated pyæmia so far as *S. aureus* is concerned.
W. D. H.

Action of Salts of the Alkaline Earths on Living Substance. N. C. PAULESCO (*Compt. rend.*, 1904, 139, 158—160).—The doses of salts of calcium, barium, and strontium necessary to prevent the formation of carbon dioxide by yeast are proportional to their

molecular weights. One molecule of such a salt produces an effect equivalent to that of one molecule of a salt of the alkalis.

W. D. H.

Behaviour of Cultures of Some Races of Yeast at Different Temperatures in Reference to Activity of the Enzymes, Length of Life, Resisting Power, and Death. WILHELM HENNEBERG (*Chem. Centr.*, 1904, ii, 52—54; from *Zeit. Spirit. ind.*, 27, 96—97, 105—106, 116—117, 126—127, 135—136, 146—147, 160—161, 173, 182—183, 194—195, 205—207, 213—214, 226, 239).—The abstract contains a description of the behaviour of some different types of yeast under varying conditions of temperature, &c., together with a brief account of the glycogen, fat, peptase, catalase, zymase, and invertin contained in the cells and the changes which these substances undergo or effect. The liability of yeasts to putrefaction and its cause is also briefly discussed.

E. W. W.

Zymase and Alcoholic Fermentation. PIERRE MAZÉ (*Compt. rend.*, 1904, 138, 1514—1517).—Zymase is widely spread in living cells both in contact with air and without air. It accumulates, however, most readily in absence of oxygen.

Zymase may be considered as being formed by the union of two diastases, one of which transforms sugar into lactic acid, the other converting lactic acid into alcohol and carbon dioxide. This is confirmed by the results of Buchner and Meisenheimer, who consider that lactic acid is an intermediate product between fermentable hexoses and alcohol.

N. H. J. M.

Variations in the Composition of Seeds during Maturation. GUSTAV ANDRÉ (*Compt. rend.*, 1904, 138, 1510—1512).—The seeds examined were white lupins, haricots, and maize. The total nitrogen increased in the dry matter during the whole period, but the percentage amounts both of nitrogen and ash are higher in very young seeds than when maturity is approached.

During maturation there is a conversion of carbohydrates soluble in water into insoluble carbohydrates saccharifiable by dilute acids.

N. H. J. M.

Mathematical Expression for the Velocity of Flow of Water through a Cell, according to Pfeffer's First and Third Schemes. W. W. LEPECHKIN (*Zeit. physikal. Chem.*, 1904, 48, 596—600).—A mathematical paper, chiefly of interest to botanists. The formula has been applied to the secretion of water in uni- and multi-cellular plants, and has given results in complete accord with the experimental data.

J. C. P.

Distribution of Some Organic Substances in Orange Flowers. EUGÈNE CHARABOT and G. LALOUE (*Compt. rend.*, 1904, 138, 1513—1514).—The greater part of the essential oil of orange flowers is contained in the petals. The formation and accumulation of odoriferous substances in the flower is most active when the flower is fully developed.

In the flowering period, the essential oil becomes richer in ethers of terpenic alcohols, in methyl anthranilate, and in total alcohol. Esterification is distinctly less complete in the flower than in the leaves and stems. The proportions of geraniol and linalool increase and diminish respectively.

The essential oil present in the proteids is very similar in composition to that of the other floral organs after the flowers have opened out; the former contains, however, rather more methyl anthranilate than the latter.

N. H. J. M.

Invertase of the Beet. MAX GONNERMANN (*Beitr. chem. Physiol. Path.*, 1904, 5, 512—514).—A question of priority in the discovery of this ferment in the sugar-beets raised by a recent paper by Stoklasa and others. It was described by the author six years ago.

W. D. H.

Lipolytic Action of the Cytoplasm of Ricinus Seed. MAURICE NICLOUX (*Compt. rend.*, 1904, 138, 1288—1291).—The saponification of fats by the cytoplasm takes place at a rate which accords with the dynamic equation for a unimolecular reaction. The cytoplasm remains unchanged during the process, but the glycerol and fatty acids produced exert a retarding action. When the quantities of cytoplasm are small, the amounts of fat saponified in a given time are proportional to the quantities of active substance present. The rate of saponification increases with the temperature up to about 35° and then decreases. Exposure to 55° for 10 minutes stops the saponification. The phenomena observed are very similar to those already noted in connection with the action of the various diastases.

H. M. D.

Hydrolysing Properties of Ricinus Seed. ED. URBAIN and L. SAUGON (*Compt. rend.*, 1904, 138, 1291—1292).—The conversion of starch into sugar and the process of inversion are both effected by the action of ricinus seed. Quantitative experiments indicate that the cytoplasm is the active constituent of the seed in both cases. The amounts of starch or sugar transformed in 24 hours are the same whether the experiments are carried out with the seed itself or with a quantity of the cytoplasm equal to that contained in the seed. The authors demonstrate further that the two processes mentioned, as well as the saponification of fatty substances, can be simultaneously effected by the action of the cytoplasm.

H. M. D.

The Lipolytic Property of the Cytoplasm of Ricinus Seed is not due to a Soluble Ferment. MAURICE NICLOUX (*Compt. rend.*, 1904, 138, 1352—1354).—The lipolytic agent, of which the cytoplasm is probably only the support, is not a ferment soluble in water, and thus differs from the known lipases. Water at once deprives the saponifying agent of its hydrolysing properties when no longer protected by the oil (compare this vol., ii, 508).

N. H. J. M.

Sulphurous Acid in Wine. I. General. WILHELM KERP (*Chem. Centr.*, 1904, ii, 56; from *Arb. Kais. Ges.-A.*, 21, 141—155).—The original paper contains a *résumé* of previous work in reference to the presence of sulphurous acid in wine, from which the results of the analyses of 1071 wines have been collected. Of these wines, 460 contained up to 0.05 gram of sulphur dioxide per litre; 366, 0.051 to 0.1; 150, 0.101 to 0.15; 63, 0.151 to 0.2, and 32 more than 0.2 gram per litre. The largest quantity detected was 0.466 gram per litre. The data show, however, that, generally speaking, wines do not contain more than 0.02 gram per litre. E. W. W.

Sulphurous Acid in Wine. II. Aldehyde-sulphurous Acid in Wine. WILHELM KERP (*Chem. Centr.*, 1904, ii, 56—57; from *Arb. Kais. Ges.-A.*, 21, 156—179).—The original paper contains a description of the properties of the acetaldehyde-sulphurous acid compound contained in wine (*Abstr.*, 1903, ii, 326). The presence of acetaldehyde in wine may be detected by means of the sodium hydrogen sulphite compound or benzeneazoformazyl; Lewin's reaction (*Abstr.*, 1900, ii, 179) is also applicable. The acetaldehyde-sulphurous acid compound is also contained in wine. In aqueous solution it is partially hydrolysed, forming sulphurous acid and aldehyde, but even in very dilute solutions the amount of decomposition is extremely small. The "free" sulphurous acid may be titrated directly with iodine solution. The velocity of combination of sulphurous acid and aldehyde depends on the concentration of the solution, and for this reason Ripper's method of determining sulphurous acid in wine (*Abstr.*, 1893, ii, 189) only gives approximate results. In fermented wines which have had only a moderate treatment with sulphur, the combined sulphur dioxide is contained in the form of the acetaldehyde compound, but in sulphurated musts and strongly sulphurated sweet wines the excess of sulphur dioxide must be assumed to be in combination with dextrose and lævulose. Since the latter compounds are more readily hydrolysed in aqueous solution, it follows that in certain cases the sulphurous acid contained in must cannot be regarded pharmacologically as identical with that contained in wine.

E. W. W.

Progressive Ripening of Cheeses. LEON LINDET and LOUIS AMMANN (*Compt. rend.*, 1904, 138, 1640—1643).—Three types of cheese, camembert, Port-salut, and gruyère, were examined with regard to the rate of degradation of the casein into soluble nitrogenous matter, and its conversion into ammonia and ammonium compounds; these changes are much more complete in the camembert than in either of the other two cheeses, the amount of soluble nitrogen after 34 days being 86.1 per cent. of the total nitrogen in the case of camembert, and only 20.2 after 49 days in the case of Port-salut, and 15.1 after 87 days in the case of gruyère.

Camembert cheese contains no lactic acid, but a small constant quantity of butyric acid (0.09 to 0.07 per cent.), due to the rapid transformation of lactose, is present throughout the ripening process.

The ripening of gruyère cheese is accompanied by an increasing proportion, 0.08 to 0.64 per cent., of the volatile fatty acids, acetic, propionic, and lactic, due to the degradation of the casein and not to the saponification of the fats, for a gruyère made from milk entirely free from cream contained the same proportions of the same fatty acids.

M. A. W.

Calcium Sulphide for Dodder and other Injurious Parasites. FÉLIX GARRIGOU (*Compt. rend.*, 1904, 138, 1549—1550).—Calcium sulphide proved to be effective in destroying animal and vegetable parasites. In dry weather, the powder must be made slightly damp.

N. H. J. M.

Complete Humic Manure. J. DUMONT (*Compt. rend.*, 1904, 138, 1429—1431).—The manure was prepared by treating a black soil, containing 2 per cent. of nitrogen, with a concentrated pearl ash solution containing aluminium phosphate. The dry matter contained: soluble humates, 50.4; insoluble substances, 49.6; organic nitrogen, 1.6; P_2O_5 , 2.9; and K_2O , 5.5 per cent.

The results of experiments in which lucerne, sugar beet, potatoes, wheat, and mangels were manured with the humic preparation (600—1000 kilos.) showed increased yields, whilst in the case of sugar beet the percentage of sugar was raised 30 per cent. It is, however, uncertain to what extent the benefit must be attributed to the humic acid and the phosphoric acid respectively.

N. H. J. M.

Analytical Chemistry.

Explosion Pipette. OTTO PFEIFFER (*Chem. Zeit.*, 1904, 28, 686).—In the pipette described, water containing 0.5 per cent. of sulphuric acid is substituted for mercury. Before the explosion, the bulk of the water is withdrawn by suction into a bulb, which is connected with the explosion bulb by a stop-cock. The explosion bulb is also provided with a stop-cock, and the platinum electrodes are specially constructed to obviate the formation of drops at the points.

A. McK.

A Comparison of Different Types of Calorimeter. THOMAS GRAY and JOSEPH G. ROBERTSON (*J. Soc. Chem. Ind.*, 1904, 23, 704—707).—The experiments described were carried out to ascertain the degree of accuracy of the results obtained by the Lewis Thompson and the William Thompson calorimeters in comparison with those yielded by combustion in compressed oxygen, the modification designed by Langbein (*Abstr.*, 1901, ii, 128) being used for the latter purpose. The values obtained by the first-mentioned instrument were

much too low, and were even untrustworthy when a correction was made for unburnt carbon. At the best the method gave only a rough estimation of the heating values of bituminous coals. It failed entirely in the case of anthracite coals. Sufficiently accurate results for practical purposes were obtained by the William Thompson calorimeter, provided that the oxygen supply was carefully regulated.

W. P. S.

Rapid Estimation of Sulphur in Iron by Evolution. S. S. KNIGHT (*Amer. Chem. J.*, 1904, 32, 84—85).—Two grams of the sample are mixed with one gram of pure reduced iron, the sulphur contents of which is accurately known, the mixture is placed in a porcelain crucible, and another gram of reduced iron is sprinkled over the top. After covering the mass with a disc of pure filter paper, the lid is put on and the whole is ignited for 10 minutes at the highest heat obtainable with the blast lamp. After this treatment, the iron will yield the whole of the sulphur as hydrogen sulphide when dissolved in hydrochloric acid. The gases evolved are passed through an ammoniacal solution of cadmium chloride, and the cadmium sulphide formed is then titrated with standard iodine as usual. L. DE K.

Estimation of Persulphates. E. PANNAIN (*Gazzetta*, 1904, 34, i, 500—504).—Hydrazine, liberated from its salts by the action of concentrated potassium hydroxide solution, reacts with the persulphates, thus: $2K_2S_2O_8 + N_2H_4 \cdot H_2SO_4 + 6KOH = 5K_2SO_4 + N_2 + 6H_2O$. Measurement in Lunge's nitrometer of the nitrogen evolved gives the amount of the persulphate. The method is simple and rapid, and is recommended by the author for checking the electrolytic preparation of persulphates. T. H. P.

Combined Sulphurous Acids. WILHELM KERP (*Chem. Centr.*, 1904, ii, 59; from *Arb. Kais. Ges.-A.*, 21, 372—376).—A description of Farnsteiner's results (compare this vol., ii, 443). E. W. W.

Occurrence of Sulphurous Acid in Dried Fruits and other Foods. H. SCHMIDT (*Chem. Centr.*, 1904, ii, 59—60; from *Arb. Kais. Ges.-A.*, 21, 226—284).—The presence of sulphurous acid in foods is best detected by acidifying the ground or macerated material with phosphoric acid and then adding a drop of very dilute iodine-starch or potassium iodate-starch solution. For quantitative determination, the sulphur dioxide should be removed by distillation. Since some natural processes interfere with the method, the results of analysis should be received with caution, and very small quantities of barium sulphate should be neglected. The behaviour of the sulphurous acid contained in dried fruit towards water and dilute alkalis shows that it is present in a combined form, probably as a dextrose compound. Proteids and cellulose are also able to combine with this acid. The presence of free sulphurous acid could not be detected with certainty in dried fruit. By exposure to the air, the fruit loses sulphur dioxide, but so slowly that for practical purposes the loss may be disregarded. In the

process of manufacture, a portion of the sulphurous acid is removed by treatment with water, and the amount lost is proportional to the quantity of water used.

E. W. W.

Estimation of Tellurium by the Electrolytic Method. G. GALLO (*Atti R. Accad. Lincei*, 1904, [v], 13, i, 713—717).—The method given by Pellini (this vol., ii, 147) for the electrolytic estimation of tellurium does not always lead to good results, and only allows of the quantitative deposition of a small quantity of that element. The following procedure yields more satisfactory results, and permits of the deposition of as much as 0.4 gram of tellurium, the error never exceeding 0.0006 gram. Pure redistilled tellurium is weighed out into a Classen crucible with a matt surface, mixed with 10 c.c. of concentrated sulphuric acid, and gently heated until the red coloration disappears and white fumes begin to be formed. When the mass is cool, a few c.c. of water, previously boiled and cooled in carbon dioxide, are carefully added and then 100—150 c.c. of 10 per cent. sodium or potassium pyrophosphate solution freed from air like the water. The liquid is then gently heated until complete solution takes place and the temperature raised to 60—62°, which must be maintained constant during the electrolysis. The anode used is a spiral of platinum wire, the normal current density being 0.025 ampere with a potential difference at the electrodes of 1.8—2 volts. The water gradually evaporating is automatically replaced by air-free water flowing down the anodic wire. A little of the pyrophosphate solution is added from time to time so as to increase gradually the volume of the liquid, the deposit of tellurium obtained thus increasing in thickness from the top to the bottom. At the conclusion of the electrolysis (Pellini, *loc. cit.*), the deposit is washed once with air-free water, or, better, with sulphurous acid solution, and then twice with absolute alcohol, after which the capsule is dried for ten minutes at 100°, cooled for at least two hours in a vacuum desiccator, and weighed: 0.025 gram of tellurium can be deposited per hour in this way.

T. H. P.

Estimation of Hydroxylamine by means of Ferric Alum and Potassium Permanganate. AUGUSTE LEUBA (*Ann. Chim. anal.*, 1904, 9, 246—248).—It has been proposed to add to a weighed quantity of hydroxylamine an excess of ferric alum and then to titrate the ferrous iron formed in the reaction. The author, having investigated the method, concludes that it is worthless, as the results may vary from 80 to 160 per cent. of the quantity actually present. The best results are obtained when operating just below the boiling point.

L. DE K.

[Detection of Minute Traces of Arsenic.] G. TODESCHINI (*Gazzetta*, 1904, 34, i, 492).—The author replies to Gautier's criticisms (*Gazzetta*, 1903, 33, i, 447) of his work on this subject (*Atti R. Ist. Veneto*, 61, 1901—1902).

T. H. P.

Detection of Arsenic in Glycerol from Soap-Lyes. MARIUS VIZERN and L. GUILLOT (*Ann. Chim. anal.*, 1904, 9, 248—251).—Fifty grams of the sample are diluted to 100 c.c. Ten c.c. of this solution are put into a tube and mixed with 2 c.c. of 10 per cent. hydrogen peroxide and 2 c.c. of hydrochloric acid. The mixture is boiled for a minute to oxidise sulphur compounds, and, when cold, introduced into a test-tube 20 cm. long and 2 c.c. wide. A piece of pure zinc weighing about 1 gram and a small fragment of copper sulphate are added, and a piece of filter paper impregnated with mercuric chloride is tied over the mouth of the tube. If after 15 minutes the interior of the paper disc assumes a pale yellow colour, the sample contains at least 1 part of arsenic per 100,000.

L. DE K.

Estimation of Boric Acid. MILTON F. SCHAACK (*J. Soc. Chem. Ind.*, 1904, 23, 699—701).—Two methods are described for the estimation of boric acid in minerals. In the first, the substance is decomposed by boiling with hydrochloric acid in a flask under a reflux apparatus. After cooling, the solution is diluted to a known volume and filtered. A definite volume of the filtrate is nearly neutralised with sodium hydroxide, using methyl-orange as indicator, and treated with 2 or 3 grams of barium carbonate. The mixture is heated for half an hour on a water-bath, cooled, and again diluted to a known volume. Iron and aluminium salts are completely precipitated by the barium carbonate. After filtering, a portion of the filtrate is neutralised exactly, using methyl-orange as indicator, and then titrated with standard alkali solution in the presence of glycerol and a little phenolphthalein.

In cases where it is desired to have the boric acid free from other substances before titration, the mineral is gently heated in a flask with a little concentrated sulphuric acid to remove carbon dioxide and volatile acids. Methyl alcohol, in quantity about 20 times that of the free sulphuric acid, is added, and the mixture distilled, a current of methyl alcohol vapour being passed into the flask during the distillation. The distillate is collected in a receiver containing water, the end of the condenser dipping below the surface of the latter. For safety the receiver is trapped with a Mohr's bulb containing water. The distillation is usually completed in 30 minutes, when the contents of the receiver and bulb are united and titrated as usual. Fluorine, when present in the mineral, must be removed before distilling. Borates, which are not decomposed by concentrated sulphuric acid, should be previously treated by suitable methods of fusion.

W. P. S.

General and Physical Chemistry.

Disappearance of the Spectral Lines of Silicon, exhibited by Certain Stars, under the Influence of the Oscillatory Spark Discharge. ARNAUD DE GRAMONT (*Compt. rend.*, 1904, 139, 188—191).—Certain lines in the silicon spectrum become very faint under the influence of self-induction introduced into the discharge circuit, and disappear completely when the self-induction is still comparatively feeble. The intensity of other lines is scarcely altered, and in some cases is very slightly increased by the self-induction. Measurements of the wave-lengths of the two classes of lines in the visible and ultra-violet part of the spectrum are recorded, and a comparison of these with stellar lines is made.

H. M. D.

Refractive Index of Solutions. C. CHÉNEVEAU (*Compt. rend.*, 1904, 139, 361—363).—The author, in reply to van Aubel, brings forward data in support of his contention that the quantity $\Delta = n - n_e$ measures the specific influence exerted by the dissolved substance on the refraction of solutions, and is proportional to its concentration, when n represents the refractive index of the solution and n_e that of the solvent calculated for its state of dilution on the basis of Gladstone's law. Data for solutions of lithium chloride in water and amyl alcohol, of ethylene bromide in propyl alcohol, and of chloral hydrate in water, ethyl alcohol, and toluene are shown to satisfy the relationship.

H. M. D.

Some Facts relating to the Observation of Variations in the Brightness of Phosphorescent Sulphides under the Action of n -Rays or Analogous Agents. E. BICHAT (*Compt. rend.*, 1904, 139, 254—256).—The author describes a number of experiments which show that the increase or diminution in the brightness of a phosphorescent screen exposed to Blondlot rays or emanations depends not only on the nature of the rays, but also on the condition of the source of the rays or of the observer in respect of electric isolation or of earth contact.

M. A. W.

The Nature of n - and n_1 -Rays, and the Radioactivity of Substances which emit these Radiations. JEAN BECQUEREL (*Compt. rend.*, 1904, 139, 264—267. Compare this vol., ii, 603).—When the Blondlot rays emitted from tempered steel, Rupert's drops, compressed wood, or insulated calcium sulphide are allowed to traverse a magnetic field normally to the lines of force, they are divided into three elements: (1) non-deviated rays which have no action on a calcium sulphide screen, but which give rise to n - or n_1 -rays when they fall on a uranium salt or a salt of poloniferous bismuth respectively; (2) rays deviated and considerably dispersed, identical with the cathode or β -rays; (3) rays deviated in the direction of the α -rays, but to a greater extent.

M. A. W.

The Refraction of n - and n_1 -Rays. JEAN BECQUEREL (*Compt. rend.*, 1904, 139, 267—270. Compare preceding abstract).—The author describes experiments which serve to show that the element of the Blondlot rays which is not deviated in a magnetic field is also that element which undergoes refraction on passing through an aluminium prism, and the refracted rays are able to combine with β - or α -rays to give rise to n - or n_1 -rays respectively. M. A. W.

Radioactive Lead, Radio-tellurium, and Polonium. ANDRÉ DEBIERNE (*Compt. rend.*, 1904, 139, 281—283).—The lead salts obtained from pitchblende from which the radium has been extracted show a very feeble radioactivity, about twice that of uranium; by repeated fractional precipitation of the lead by means of hydrochloric acid, a residue is obtained from which a small quantity of basic bismuth nitrate can be precipitated which has all the characteristics of poloniferous bismuth, its radioactivity being about 100,000 times that of uranium, and consisting, like polonium, of homogeneous, slightly penetrating rays, difficultly deviable in the magnetic field (compare Curie, Abstr., 1900, ii, 126). Further, the radioactive substance possesses all the characteristic properties of Marckwald's radio-tellurium (compare Abstr., 1903, ii, 81, 733), giving a slight precipitate with stannous chloride and a slight deposit on a sheet of bismuth, each of which is very strongly radioactive. The author concludes, therefore, that the radioactive substance obtained as above, radioactive lead (compare Hofmann and Strauss, Abstr., 1901, ii, 19, 159, 385, 655; 1902, ii, 79, 261, 397; 1903, ii, 402), and radio-tellurium are identical with the element polonium (compare Giesel, Abstr., 1902, ii, 78, 208; 1903, ii, 20), which is the only radioactive substance in pitchblende capable of being precipitated by hydrogen sulphide in acid solution. M. A. W.

Molecular Attraction. J. E. MILLS (*J. Physical Chem.*, 1904, 8, 383—415).—A continuation of the previous paper (Abstr., 1902, ii, 596). The author briefly reviews the assumptions on which he bases the hypothesis that the internal latent heat is solely spent in changing the distances between the molecules, and points out that no assumption is made which has not been frequently accepted or assumed by leading physical chemists. If the molecular attraction obeys the law of inverse squares, the internal latent heat for each substance should be $K(\sqrt[3]{d} - \sqrt[3]{D})$, where d , D are the densities in the liquid and gaseous states. In the present paper, the author has calculated the value of the internal latent heat at various temperatures from the temperature coefficient of the vapour pressure, employing the vapour pressure data of Ramsay and Young. The ratio of these values to the values of $(\sqrt[3]{d} - \sqrt[3]{D})$ were then found for temperatures from 0° to the critical temperature. Twenty-one compounds were investigated and in almost all cases the ratio was as constant as the experimental errors would allow. In the case of water, the alcohols, and acetic acid, it was not expected that constancy would be obtained on account of association; except in the case of acetic acid, constant values were obtained, however, and this, in the author's

opinion, indicates that the association is due to the molecular attraction. Only in the case of stannic chloride was the variation of the constant (26.2 at 0° , 22.15 at 280°) greater than that due to errors of experiment. The author hence considers that the law of inverse squares is established for molecular attraction.

L. M. J.

Properties of Substances regarded as Functions of the Space Occupied by their Atoms and Molecules. Systematic Classification of the Elements. ISIDOR TRAUBE (*Zeit. anorg. Chem.*, 1904, 40, 372—384).—The physical and chemical properties of elements and compounds depend primarily on the space occupied by their atoms and molecules. The latter factor has a much greater influence on the general properties of substances than the atomic weight has. The relation between volume and pressure, hardness, expansion by heat, melting point, boiling point, surface tension, specific heat, valency, and other properties is discussed. If the volume of a substance at two different temperatures is known, it should be possible to describe its physical and chemical properties not only qualitatively, but to a large extent quantitatively; this would not be possible if the atomic weight only of the substance was known. The question is raised as to whether it would not be more convenient to regard the atomic weight as a function of the atomic volume instead of the converse view, commonly accepted.

A. McK.

Diffusion of Argon and Helium. RUDOLF SCHMIDT (*Ann. Physik*, 1904, [iv], 14, 801—821).—With a modification of the Maxwell-Loschmidt method, the diffusion coefficient for the two gases, argon—helium, has been found to be 0.25405 at 15° and 760 mm. pressure, and the value calculated by Meyer's formula agrees very closely with this, only, however, so long as the numerical ratio of the molecules of the two gases is equal to unity.

J. C. P.

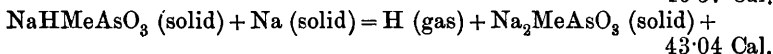
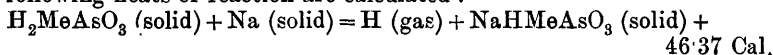
Stability of the Equilibrium of Bivariant Systems. PAUL SAUREL (*J. Physical Chem.*, 1904, 8, 436—439).—The following theorem is established. If in a univariant system of $n+1$ phases at constant pressure and temperature a reversible change which increases the entropy causes the i -th phase to increase, then the bivariant system in which this phase is missing cannot exist in stable equilibrium at the given pressure at a higher temperature, nor at the given temperature at a greater pressure.

L. M. J.

Equilibrium $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$. O. HAHN (*Zeit. physikal. Chem.*, 1904, 48, 735—738).—In a previous paper (Abstr., 1903, ii, 274), the author arrived at an equation connecting K , the equilibrium constant of the above reaction, with T , the absolute temperature, and showed that the calculated values of K agreed well with the observed values, except at high temperatures. If, however, the actual molecular heats (constant pressure) as calculated by Le Chatelier (*Zeit. physikal. Chem.*, 1887, 1, 456) are taken instead of the mean molecular heats (constant volume), better agreement is obtained. The equation for K then becomes $\log K = -2226/T - 0.0003909T + 2.4506$.

J. C. P.

Thermochemistry and Acidimetry of Methylarsonic Acid. A. ASTRUC and E. BAUD (*Compt. rend.*, 1904, 139, 212—215).—Addition of one molecule of sodium hydroxide to one molecule of methylarsonic acid, H_2MeAsO_3 , in dilute aqueous solution develops 15.43 Cal., a second molecule of the hydroxide develops 11.93 Cal., whilst the addition of a third molecule produces no thermal effect. The heats of solution of methylarsonic acid and of the anhydrous monosodium and disodium salts (1 mol. in 6 litres) are respectively -2.86 Cal., +8.60 Cal., and +19.89 Cal. From these numbers, the following heats of reaction are calculated :



Methylarsonic acid is monobasic towards litmus or rosolic acid and dibasic towards Poirrier blue (compare Abstr., 1902, ii, 370).

The monosodium salt crystallises with $3\text{H}_2\text{O}$, and the disodium salt with $6\text{H}_2\text{O}$, the heat of hydration of the latter being +24.36 Cal.

H. M. D.

Heat of Formation of Antimony Trisulphides. JOSEPH GUINCHANT and PAUL CHRÉTIEN (*Compt. rend.*, 1904, 139, 288—289. Compare this vol., ii, 568).—A reply to Berthelot (compare this vol., ii, 605).

M. A. W.

Catalytic Reactions at High Temperatures and Pressures. VIII. WALDIMIR N. IPATIEFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 786—813; *Ber.*, 1904, 37, 2961—2985. Compare Abstr., 1903, i, 453, 593, 594, 595, and 598).—Investigation of the decomposition of alcohols at high temperatures and pressures, in the presence of iron as catalyst, leads to the conclusion that increase of pressure diminishes the decomposability of alcohols, and although the course of the reaction is the same as under the ordinary pressure, yet the products of the reaction—especially the gases formed—differ in composition from those obtained under atmospheric pressure. The substances examined were methyl, ethyl, propyl, and amyl alcohols, aldehyde, isopropyl alcohol, acetone, and dimethylethylcarbinol.

The decomposition of primary, secondary, and tertiary alcohols differs as regards both the products formed and the velocity, which may be taken as approximately proportional to the rate of increase of pressure. Curves showing the increase of pressure with time were constructed and the maximum values of dP/dT determined; it is found that the product of this maximum value, with the time after which it is arrived at, is a constant: $(dP/dT)_{\text{max.}} \cdot T = \text{a constant} = R$. This constant R holds moderately well, not only at different temperatures for one and the same alcohol, but for all primary alcohols, and may serve as roughly representing the relative amounts of energy transformed by different catalysts in the complete decomposition of organic compounds.

The geometrical representation of the above relation will be a rectangular hyperbola, in which the product of the co-ordinates is a

constant. For primary alcohols, the value of R is about 800 (using the atmosphere and minute as units), and in the decomposition two processes take place: (1) formation of hydrogen and aldehyde and (2) resolution of the latter into a saturated hydrocarbon and carbon monoxide. For secondary alcohols and for aldehydes (where only one reaction takes place) the value of R is only half as great.

In the decomposition of primary and secondary alcohols in presence of catalytic iron under high pressures, no separation of carbon is observed such as is met with under the ordinary pressure, and all alcohols at high temperatures undergo a special decomposition, to which the name paraffinoid may be given, as the gases formed consist mainly of saturated hydrocarbons.

T. H. P.

Catalytic Reactions at High Temperatures and Pressures. Dissociations in the Phenomena of Catalysis. IX. WLADIMIR N. IPATIEFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 813—835; *Ber.*, 1904, 37, 2986—3005. Compare preceding abstract).—Investigation of the decomposition, in presence of alumina as catalytic agent, of alcohols in closed vessels under high pressures and at definite temperatures shows that the alcohols undergo decomposition into olefines and water, just as is the case under the ordinary pressure; the temperatures at which the catalytic decompositions occur are, however, higher than under atmospheric pressure. But it is found that, at temperatures lower than those at which the olefines are formed from primary alcohols, one molecule of water is given up by two molecules of alcohol, an ether being formed. This reaction is reversible, the ether again yielding the alcohol under the influence of alumina. At higher temperatures, the ether undergoes further decomposition into olefine and water. At still higher temperatures, the olefine, and also the aldehyde formed by the hydration of the ether, are decomposed, yielding gaseous products partially similar to those formed during catalysis by iron.

The pressure curves for certain primary, secondary, and tertiary alcohols and ethyl ether have been constructed and the values of R determined free (preceding abstract); these are found to have about half the corresponding values for catalysis with iron.

Moreover, under the ordinary pressure, ethyl ether is formed in the decomposition of ethyl alcohol, but only in very small quantities; in the same way, ethyl alcohol is always formed in the catalytic decomposition of ether under the influence of alumina under the ordinary pressure.

T. H. P.

Question of the Accurate Determination of Molecular Weight from the Vapour Density. MAX REINGANUM (*Zeit. physikal. Chem.*, 1904, 48, 697—712).—In reference to Ramsay and Steele's paper dealing with this subject (*Abstr.*, 1903, ii, 635), the author shows that with the help of his own equation of condition for gases under low pressures (*Ann. Physik*, 1901, [iv], 6, 533), the data obtained by these workers and those obtained for isopentane by Young (*Abstr.*, 1899, ii, 633) give very good values for the molecular weight. Further, with the aid of the law of corresponding conditions, it is shown that the results of Ramsay and Steele are in harmony with

those of Young, so far as the extent of the deviations from the gas laws exhibited by vapours is concerned. As shown in the paper, these deviations may be very simply measured by the use of Hoffmann's method. J. C. P.

Determination of Vapour Density from Increase of Pressure and the Accuracy of this Method as compared with that of Known Methods. W. HAUPT (*Zeit. physikal. Chem.*, 1904, 48, 713—724).—The author describes an apparatus, consisting essentially of a glass globe provided with a brass cap and connected with a manometer, which permits the measurement of the increase of pressure caused by the vaporisation of a known weight of a liquid in a given space. The liquid is contained in a small glass bottle and placed until required in an air-tight chamber attached to the brass cap. The accuracy obtainable by this method is shown to be in no way inferior to that of the other known methods [compare Lumsden's method, *Trans.*, 1903, 83, 342, to which no reference is made]. J. C. P.

Melting Point Diagram for Mixtures of N_2O_4 and NO . N. M. WITTORFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 857—863).—On saturating liquid nitrogen peroxide with nitric oxide and subsequently cooling the solution, dark blue crystals of nitrous anhydride melting at -103° separate; no other compound is formed. The eutectic mixture of N_2O_4 and N_2O_3 melts at -112° . It is probable that nitric oxide does not dissolve nitrous anhydride, but that the relation between them is similar to that between water and benzoic acid. T. H. P.

Relative Viscosity of Liquids. KARL BECK (*Zeit. physikal. Chem.*, 1904, 48, 641—681).—By a method of which full details are given, the viscosity of fresh human blood has been determined and at 38° found to be about five times as great as that of water.

The viscosities of a number of compounds have been determined at temperatures just above their freezing points in order to study the effect of differences in constitution. The viscosity constants of the isomorphous compounds, dibenzyl, azobenzene, benzylideneaniline, benzylaniline, and stilbene are very closely related. For isomorphous mixtures of these compounds, the viscosity varies in a linear manner provided the freezing point is the same as that calculated by the mixture rule. In cases where the latter condition is not fulfilled, the viscosity curve exhibits a maximum where the freezing point curve has a minimum.

Study of the viscosity shows that inactive mixed crystals of optical antipodes break up on melting into a mixture of the two antipodes. The two racemic compounds, tartaric acid and methyl diacetyltartrate, have been shown to break up similarly on melting, so that the melting point is also a transition point.

The behaviour of the oximes of benzaldehyde and anisaldehyde supports the view that the α -oximes occur in two monotropic forms, of which the one with the lower melting point has been obtained through the hydrate.

The two liquids obtained by melting the monotropic forms of iodine

monochloride are exactly the same so far as the viscosity constant is concerned.

J. C. P.

Fluidal Metals. P. DUHEM (*J. Chim. Phys.*, 1904, ii, 438—446).—It has been shown by Spring (this vol., ii, 313) that metals under great compression assume an allotropic form, which he terms the “fluidal” metal (*métal flué*) as distinct from the ordinary form obtained by cooling the molten metal, which he terms the “annealed” metal (*métal recuit*). As annealed and fluidal bismuth form a couple in which the fluidal metal is the cathode, it follows that at the ordinary temperature and pressure the fluidal bismuth is in true equilibrium and the annealed bismuth in pseudo-equilibrium. At high temperatures, however, the fluidal metal is transformed into the annealed, whilst under high pressures the annealed form passes into the fluidal bismuth, the transformation of annealed to fluidal bismuth being accompanied by the development of heat. From these data, it is clear that the equilibrium curve between the two forms, when represented as a diagram with pressure ordinates and temperature abscissæ, consists of a curve ascending from left to right and cutting the axis of zero pressure at an elevated temperature. On each side of this curve lie the fields of pseudo-equilibrium, and beyond the regions of transformation. For other metals, if the reversible transformation is endothermic, the curve will be of the same form, but for all examined hitherto they cut the horizontal axis ($T=0$) under an elevated pressure. If the transformation is endothermic, the curve descends from left to right.

L. M. J.

Hard and Soft States in Metals. G. T. BEILBY (*Electro-Chem. Metall.*, 1904, 3, 806—819. Compare *Proc. Roy. Soc.*, 1902, 72, 218—225; *J. Soc. Chem. Ind.*, 1903, 1166—1177).—In continuation of previous work, the author brings forward evidence showing that metals occur ordinarily in two distinct solid phases: (1) the hardened or amorphous phase; (2) the annealed or crystalline phase. The former is converted into the latter by the agency of heat, the latter into the former by mechanically produced flow. The photomicrographs obtained make it probable that two intermediate mobile phases also exist. In this study of the phenomena of hardening and softening, both malleable ductile metals, such as gold, silver, platinum, copper, and lead, and brittle crystalline metals, such as antimony and bismuth, have been investigated, and it is found that flow takes place in all cases. As shown in detail for the case of silver, the different mechanical, optical, electrical, and thermochemical properties associated with the hard and soft forms of metals respectively group themselves on either side of a transition temperature common to all, hence these two forms of a metal may be regarded as two distinct phases. The transformation from hard to soft is thermally irreversible, that is, mere lowering of the temperature below the transition point does not bring about the reverse change from soft to hard. Hardening, on the other hand, occurs whenever work is done on the crystalline phase, and, as shown by the photomicrographs, this hardening is accompanied by the disappearance of crystalline, and the appearance of vitreous and granular

character. This effect is strictly confined to the surface in cases where the hardening has been produced by polishing, but extends to a greater depth where the mechanical treatment has consisted in beating, rolling, or pressing. When a piece of metal is strained, there is relative displacement and mutual friction of the crystalline grains, resulting in the formation of an encasing network of the hardened phase. Thus the tensile strength of a wire increases when its diameter is reduced by drawing. The transition temperatures referred to above have been approximately determined by a softening test, with the following results: silver began to soften at 230° , and was completely soft at 265° ; the two corresponding temperatures found for gold were 250° and 280° ; for copper, 250° and 290° ; for magnesium, 300° and 360° .

J. C. P.

The Permanence of Crystallitic Forms in Crystals. FLORIS OSMOND and G. CARTAUD (*Compt. rend.*, 1904, 139, 404—406).—The lack of homogeneity in microsections of bronzes containing 9—10 per cent. of tin, when treated with a suitable etching fluid, has been explained on the basis of the laws of solidification of solutions. The sharpness of the crystalline contours is, however, difficult to account for, and the authors point out that the mechanical operations involved in the production of the section contribute to produce the appearances observed. A method of preparing sections is described in which the disturbing effects of the mechanical operations are eliminated.

H. M. D.

The Fundamental Law of Osmotic Phenomena. E. ARIÈS (*Compt. rend.*, 1904, 139, 196—198).—A simple thermodynamic proof is given, showing that, if a solution at a given temperature and under a pressure p_1 is in osmotic equilibrium with the pure solvent at the same temperature and under a pressure p_2 , the thermodynamic potential of the pure solvent is the same as that of the solvent in the solution (compare this vol., ii, 16).

H. M. D.

Theory of Dilute Solutions based on the Law of van't Hoff. E. ARIÈS (*Compt. rend.*, 1904, 139, 401—404).—Making use of the fundamental law of dilute solutions, the author deduces, in a simple manner, values for the thermodynamic potential of the solvent and the dissolved substance present in a solution.

H. M. D.

Some Physical Constants of Saturated Solutions. I. EARL OF BERKELEY (*Phil. Trans.*, A, 1904, 203, 189—215).—The densities and solubilities of the following salts have been determined at temperatures between 0° and the boiling points of the saturated solutions: chlorides, sulphates, and nitrates of sodium, potassium, rubidium, caesium, and thallium, also potassium, rubidium, caesium, and thallium alums. Full details are given of apparatus and methods.

J. C. P.

The Constitution of Dissolved Salts. ALBERT COLSON (*Compt. rend.*, 1904, 139, 199—201).—The phenomena observed on precipita-

ting zinc sulphate solutions with alkali cannot be completely explained in a satisfactory manner on the assumption that the dissolved sulphate is represented by the formula ZnSO_4 .

When baryta is gradually added in excess to a zinc sulphate solution, the ordinary equation, $\text{ZnSO}_4 + \text{Ba}(\text{OH})_2 = \text{BaSO}_4 + \text{Zn}(\text{OH})_2$, does not represent the actual facts observed (compare this vol., ii, 377 ; ii, 532). The dissolved zinc sulphate (copper sulphate behaves similarly) apparently behaves like a weak acid and dissolves zinc hydroxide ; to account for this, the author proposes that the dissolved salt should be represented by a formula of the type $\text{H}\cdot\text{SO}_4\cdot\text{Zn}\cdot\text{OH}$. The fact that the precipitate which separates from solution on addition of baryta contains 1 mol. ZnSO_4 for 3 mols. BaSO_4 leads the author to double this formula, and the dissolved zinc sulphate is then represented by $\text{H}\cdot\text{SO}_4\cdot\text{Zn}\cdot\text{O}\cdot\text{Zn}\cdot\text{SO}_4\cdot\text{H}$, a complex molecule containing two hydrogen atoms with acid functions.

H. M. D.

Modification of the Freezing Point Method. STEWART W. YOUNG and W. H. SLOAN (*J. Amer. Chem. Soc.*, 1904, 26, 913—922).—In the authors' method, the stirrer consists of a cylinder of ice by means of which the pure solvent (water) is agitated whilst its melting point is taken ; a known weight of the solute is then added, the solution obtained is thoroughly stirred with the ice stirrer, whilst the vessel containing the solvent is surrounded by a freezing mixture. The temperature is read when equilibrium is reached, the thermometer and ice stirrer being then removed. The freezing vessel, which is an ordinary cylindrical vacuum jacket, is taken from the freezing mixture and weighed, and as the weight of the solute is known, that of the solvent is obtained. A series of determinations with increasing concentration may be made by successively adding more of the solid, stirring in each instance with the ice stirrer and again noting the temperature and weight as before. The principle is thus somewhat similar to that adopted in Landsberger's boiling point apparatus. A mechanical method for agitating the stirrer was employed.

W. A. D.

Concentration of Metallic Ions in Silver Nitrate Solutions containing Albumin. G. GALEOTTI (*Zeit. physiol. Chem.*, 1904, 42, 330—342).—The concentration of the metallic ions in a silver nitrate solution containing albumin has been determined by the Poggendorf-Ostwald method, using the equation $\log C_k = \log C_o - E/0.0575$, where C_k is the concentration required, C_o the concentration of silver ions in an $N/10$ solution of silver nitrate, and E the *E.M.F.* of a concentration cell, using the solution under investigation, $N/10$ silver nitrate and silver electrodes, the two solutions being connected by a strip of dry filter paper.

The results show that the presence of egg-albumin considerably lessens the number of silver ions ; the concentration of these ions is extremely low when the system consists of a single phase (solution and no precipitate), but is much higher when the system consists of two phases (solution and precipitate.).

If the amounts of water and silver nitrate are kept constant in a

series of experiments and the amount of albumin varied, the concentration of the silver ions diminishes rapidly and according to a fixed law for small amounts of albumin; a sharp break then occurs and the concentration of the silver ions diminishes less rapidly as the albumin is increased and approximates a limiting value, which is the same however large the amount of albumin present may be. The results may be represented in the form of a curve with $\log C_k$ and amounts of albumin as ordinates.

The law governing the relationships of the concentrations of albumin, silver nitrate molecules, and silver ions in a two-phase system can readily be derived, by the aid of Jahn's equation (Abstr., 1902, ii, 597), when account is taken of the mutual actions of the dissolved molecules. These mutual actions are so considerable that they considerably modify the solubility of the albumin and the ionisation of the silver nitrate.

J. J. S.

Toxins and Antitoxins from the Physico-chemical Point of View, and the Laking of Red Corpuscles. HANS KOEPPE (*Pflüger's Archiv*, 1904, 103, 140—148. Compare Abstr., 1903, ii, 736; Arrhenius and Madsen, *ibid.*, 561).—Attention is drawn to the fact that Arrhenius and Madsen's method led to a number of experimental errors which the author had not encountered in similar researches. It is shown that these were largely due to the fact that the hæmolytic agent or alkali was added to the blood emulsion instead of *vice versa*.

The author adheres to the conclusion that laking in alkaline liquids is due to the concentration of hydroxyl ions in such solutions.

J. J. S.

Flocculation of Colloids and Bacteria Agglutination. H. BECHHOLD (*Zeit. physikal. Chem.*, 1904, 48, 385—423).—The rate of flocculation depends, within certain limits, on the concentration. When the concentration decreases to a certain point, flocculation practically ceases; whilst above a certain degree of concentration the rate of flocculation is more or less independent of concentration.

There is no essential difference between the flocculation of bacteria and colloids, &c.

The flocculation of unorganised suspensions is hindered by colloids (gelatin, &c.). This is not due to increased viscosity, but to the particles becoming enveloped by the colloid. The suspensions then behave like colloids.

Bacteria, like all true suspensions, travel to the anode.

N. H. J. M.

Agglutination. WILHELM BILTZ (*Zeit. physikal. Chem.*, 1904, 38, 615—623).—It is proposed to prepare mixtures of inorganic colloids with agglutins and with bacteria respectively, and to ascertain whether these substances act in accordance with the observations of Eisenberg and Volk (*Zeit. Hygiene*, 1902, 40, 155. Compare also Arrhenius, Abstr., 1903, ii, 356). It should also be ascertained whether inorganic colloids exist which behave like antitoxins.

N. H. J. M.

New Electric Furnace and Various Other Electric Heating Appliances for Laboratory Use. HARMON N. MORSE and J. C. W. FRAZER (*Amer. Chém. J.*, 1904, 32, 93—119).—In attempting to devise a method for the direct measurement of osmotic pressure (Abstr., 1901, ii, 543 ; 1902, ii, 553 ; 1903, ii, 272), considerable difficulty has been experienced in the production of a suitable osmotic cell. It has been found that the failure of these cells is largely due to the production of comparatively large channels in the wall by the escaping steam during the baking of the clay. In order to avoid the formation of these channels, it is necessary that the temperature should be very carefully regulated during the period in which the clay loses most of its water. An electric furnace has therefore been devised for baking the cells, which is capable of being maintained at any desired temperature, and a smaller form has been designed for ordinary laboratory purposes, such as the fusion of silicates in crucibles. The furnace is calibrated by determining its resistance for all temperatures up to the maximum required, in order that it may be possible to maintain any desired temperature or to ascertain at any time the temperature attained. The furnace described by the authors was calibrated for temperatures between 383° and 967°. A detailed description of the furnace and the method of constructing it is given and illustrated with diagrams.

An accurately calibrated electric furnace is well adapted for the study of reactions at high temperatures, but in order to obtain a high degree of accuracy it is necessary to reduce as far as possible the length of time required to establish equilibrium between the temperature within the furnace and that of the external air. This can be accomplished by coating the outside of the furnace with graphite, a substance which conducts electricity and the conductivity of which increases with rise of temperature. The circuit is divided, so that whilst the greater part of the current passes through the furnace, another portion passes over and heats the surface in contact with the air. By this means, compensation is automatically made for the increased loss of heat to the external air which attends any rise in the temperature of the furnace, for as the temperature rises the conductivity of the circuit through the furnace diminishes, whilst that of the outer circuit increases, and a larger proportion of the current therefore takes the latter course. This principle has been applied in the construction of graphite stoves for use as hot air-baths, a furnace for heating sealed tubes, and a bath with platinum stove for heating rather large vessels at any temperature up to 500°. For the details of these various forms of apparatus, the description and diagrams in the original must be consulted.

E. G.

Apparatus for the Determination of High Melting Points. FR. KUTSCHER and OTORI (*Zeit. physiol. Chem.*, 1904, 42, 193—194).—The apparatus consists essentially of a double-walled air-bath. The thermometer and tube with substance are fitted into a glass test-tube and this is placed in a silica flask which can be heated either directly or on asbestos. If the tube containing the substance is made wide and

of a conical shape, temperatures of explosion may be determined without risk. J. J. S.

Press for the Preparation of Pellets. PAUL FREUNDLER (*Bull. Soc. chim.*, 1904, [iii], 31, 815—816).—In the screw presses in general use for the preparation of pellets for physico-chemical determinations, the piston is apt to become twisted after a time, so that it no longer fits accurately into the mould. It is proposed to remedy this defect by inserting, between the head of the piston and the end of the screw by which the pressure is applied, a cross-piece which slides vertically on the frame of the press. By this means, direct contact of the screw with the piston is avoided and the latter remains perfectly vertical. The apparatus is figured in the original. T. A. H.

Inorganic Chemistry.

Viscosities of Oxygen, Hydrogen, Chemically Pure and Atmospheric Nitrogen, and the change of these with the Temperature. HERMANN MARKOWSKI (*Ann. Physik*, 1904, 14, 742—755).—The viscosity coefficients of oxygen, hydrogen, and nitrogen have been determined at temperatures between 0° and 183° by a method similar to that employed by Schultze (*Ann. Physik*, 1901, [iv], 5, 140) and Breitenbach (*ibid.*, 166). The variation of the coefficient with temperature is given satisfactorily by Sutherland's formula. Except in the case of hydrogen, the temperature-coefficient of the viscosity constant diminishes as the temperature rises. The viscosity constant for atmospheric nitrogen can be satisfactorily calculated from those for argon and chemically pure nitrogen with the aid of Pulong's formula. J. C. P.

Absorption of Gases by Wood Carbon at Low Temperatures. Sir JAMES DEWAR (*Compt. rend.*, 1904, 139, 261—264).—The power of absorption of cocoa-nut charcoal for gases (compare Dewar and Tait, *Proc. Roy. Soc. Edin.*, 1875, 8, 348) is largely increased at the temperature of liquid air, and the coefficient of absorption at this temperature has been determined; for this purpose, the charcoal is placed in a small glass tube supplied with a stopcock, the air is removed from the tube and charcoal by means of an air pump, and the stopcock closed, the tube is then placed in a liquid air calorimeter, and connected with a graduated vessel containing the gas under investigation; the stopcock is opened and the amount of gas absorbed and the heat developed in the process are measured; the results are embodied in the following table:

| | Volume absorbed at 0°. | Volume absorbed at -185°. | Heat developed in gram-calories. |
|-----------------------|------------------------------|---------------------------------|--|
| Hydrogen | 4 c.c. | 135 c.c. | 9.3 |
| Nitrogen | 15 " | 155 " | 25.5 |
| Oxygen | 18 " | 230 " | 34 |
| Argon..... | 12 " | 175 " | 25 |
| Helium | 2 " | 15 " | 2 |
| Electrolytic gas..... | 12 " | 150 " | 17 |
| CO + O | 30 " | 195 " | 34.5 |
| Carbon monoxide | 21 " | 190 " | 27.5 |

When cocoa-nut charcoal, at -185° , is saturated with pure dry air, it absorbs the oxygen more readily than the nitrogen, the gas recovered at 15° containing 56 per cent. of oxygen; further, if the absorbed gas is allowed to escape gradually, it is possible to effect a partial separation of the two constituents, the first fraction containing 18.5 and the sixth 84.0 per cent. of oxygen. M. A. W.

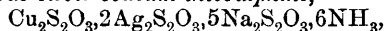
The State of Vaporised Carbon. MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1904, [viii], 2, 185—192).—A *résumé* of work already published (compare this vol., ii, 27). M. A. W.

Preparation of Sulphurous Acid for Use as a Reagent. LOUIS L'HÔTE (*Ann. Chim. anal.*, 1904, 9, 305).—A washed current of sulphur dioxide generated from charcoal and sulphuric acid is passed into a small bottle previously heated, and by means of a funnel boiling water is introduced and the delivery tube is gradually withdrawn. After the bottle is completely filled and saturated with the gas, it is at once closed.

In this manner, a solution is obtained perfectly free from sulphuric acid. L. DE K.

Complex Thiosulphates. OWEN LOUIS SHINN (*J. Amer. Chem. Soc.*, 1904, 26, 947—952).—On adding concentrated aqueous sodium thiosulphate to an ammoniacal solution of a copper salt, a blue, crystalline substance separates, which seems to be an *ammonio-cuprous sodium ammonium thiosulphate*, $3\text{Cu}_2\text{S}_2\text{O}_3 \cdot 4\text{Na}_2\text{S}_2\text{O}_3 \cdot (\text{NH}_4)_2\text{S}_2\text{O}_3 \cdot 6\text{NH}_3$, as it is also obtained by the addition of aqueous sodium thiosulphate to cuprous oxide dissolved in ammonia; when dry, it is moderately stable in the air, but when moist it rapidly oxidises. It is partly decomposed by water.

Ammonio-cuprous silver sodium thiosulphate,



obtained by adding aqueous sodium thiosulphate to a solution of mixed copper and silver salts in ammonia, crystallises in tetragonal pyramids ($a:c=1:0.8375$) and appears to be isomorphous with the foregoing salt. W. A. D.

Reaction between Carbon Dioxide and Soluble Nitrites. RICHARD B. MOORE (*J. Amer. Chem. Soc.*, 1904, 26, 959—961).—As bearing on the controversy between Meunier and Marie and Marquis

(compare this vol., i, 208; ii, 252, 333), it is shown that carbon dioxide carries off nitrous acid when passed through a solution of potassium or sodium nitrite (compare Moody, *Proc.*, 1903, 19, 240).

W. A. D.

Action of Ammonia on Boron Bromide and on Phosphorus Trichloride. ALEXANDRE JOANNIS (*Compt. rend.*, 1904, 139, 364—366. Compare Abstr., 1903, ii, 140).—When dry ammonia acts on boron bromide at 0°, borimide is produced according to the equation $2\text{BBr}_3 + 27\text{NH}_3 = 6(\text{NH}_4\text{Br}, 3\text{NH}_3) + \text{B}_2(\text{NH})_3$. If the temperature is allowed to rise to 20°, the ammoniacal ammonium bromide dissociates, and 9 mols. of ammonia are evolved for each molecule of boron bromide used.

When the vapour of phosphorus trichloride is led by means of a current of dry hydrogen into liquefied ammonia at -78° , the following reaction takes place:



The constancy of the reacting proportions points to the formation of the amino-imino-compound, but the product may be a mixture of the amide and the imide. When the temperature rises to 0°, the ammoniacal complex dissociates, and 9 mols. of ammonia are evolved for each mol. of the phosphorus trichloride. Between 0° and 100°, a further quantity of ammonia is evolved (1 mol. for 2 mols. PCl_3), corresponding with the equation $2\text{NH}:\text{P}:\text{NH}_2 = \text{NH}_3 + \text{P}_2(\text{NH})_3$.

H. M. D.

Melting Points of Mixtures of the Alkaline Earths with Boric Anhydride. W. GUERTLER (*Zeit. anorg. Chem.*, 1904, 40, 337—354. Compare this vol., ii, 610, 614).—The melting point curves of calcium, strontium, and barium oxides respectively with boric anhydride are represented. Curves are also shown to represent the concentration of the molten masses of mixtures of those oxides saturated with boric anhydride at temperatures varying from 0° to 1400°. The author was unable to confirm the existence of Ditte's compounds, $2\text{MO}, 3\text{B}_2\text{O}_3$ and $3\text{MO}, 2\text{B}_2\text{O}_3$. When concentrations corresponding to the compounds $2\text{CaO}, 3\text{B}_2\text{O}_3$, $2\text{SrO}, 3\text{B}_2\text{O}_3$, $2\text{BaO}, 3\text{B}_2\text{O}_3$ are chosen, the crystallisation takes place almost at a constant temperature with the formation of a eutectic mixture. The author's results, however, confirm the existence of Ditte's compounds, $2\text{CaO}, \text{B}_2\text{O}_3$ and $2\text{SrO}, \text{B}_2\text{O}_3$. Calcium diborate and strontium diborate show a very slight tendency to crystallise spontaneously; barium diborate could not be obtained crystalline.

The existence of the metaborates, CaB_2O_4 , SrB_2O_4 , and BaB_2O_4 , is confirmed. Calcium metaborate and strontium metaborate crystallise in long needles exhibiting double refraction, whilst barium metaborate forms flat prisms. Calcium, strontium, and barium pyroborates form finely-crystalline, marble-like masses.

The existence of barium orthoborate was proved.

The following borates are capable of existence:

| | Mg. | Ca. | Sr. | Ba. |
|--------------|-------------------------------------|---|---|-------------------------------------|
| Orthoborate | $3\text{MgO}, \text{B}_2\text{O}_3$ | $(3\text{CaO}, \text{B}_2\text{O}_3) ?$ | $(3\text{SrO}, \text{B}_2\text{O}_3) ?$ | $3\text{BaO}, \text{B}_2\text{O}_3$ |
| Pyroborate | $2\text{MgO}, \text{B}_2\text{O}_3$ | $2\text{CaO}, \text{B}_2\text{O}_3$ | $2\text{SrO}, \text{B}_2\text{O}_3$ | $2\text{BaO}, \text{B}_2\text{O}_3$ |
| Metaborate | — | $\text{CaO}, \text{B}_2\text{O}_3$ | $\text{SrO}, \text{B}_2\text{O}_3$ | $\text{BaO}, \text{B}_2\text{O}_3$ |
| Diborate ... | — | $\text{CaO}, 2\text{B}_2\text{O}_3$ | $\text{SrO}, 2\text{B}_2\text{O}_3$ | $\text{BaO}, 2\text{B}_2\text{O}_3$ |
| | | | | A. McK. |

Action of Water and Saline Solutions on Certain Slightly Soluble Phosphates. FRANK K. CAMERON and L. A. HURST (*J. Amer. Chem. Soc.*, 1904, 26, 885—913).—Water does not dissolve the phosphates of trivalent iron, aluminium, and calcium as such, but hydrolyses them to a slight extent; the action takes place slowly, so that in none of the experiments recorded, even although in some cases the phosphate was shaken with water for 30—80 days, was a final condition of equilibrium attained. Free acid accumulates in the solution, whilst the corresponding base is largely precipitated. Although the phosphoric acid in solution tends to increase the solubility of the phosphate, the small amount of dissolved base appears to exercise a greater influence in the opposite direction, so that the addition of increasing amounts of water produces a relatively smaller, although actually larger, decomposition of the phosphate. The diminution in solubility of calcium phosphate caused by the presence of calcium chloride or nitrate corresponds with this view of the foregoing changes, but the increased solubility of aluminium and ferric phosphates caused by aluminium and iron salts respectively (Schneider, *Abstr.*, 1893, ii, 573; 1895, ii, 112) is not in accord with it, unless one assumes that in this case the free acid produced by the hydrolysis of the added salts aids the decomposition.

The presence of potassium chloride decreases the amount of phosphoric acid split off by water from ferric, aluminium, or calcium phosphate, but increases the quantity of iron, aluminium, or calcium entering into solution. Potassium sulphate, on the other hand, increases the amount of phosphoric acid in the case of ferric phosphate, but diminishes it in that of aluminium phosphate. Sodium nitrate diminishes the amount of acid hydrolysed from ferric and aluminium phosphates, but appears to cause an increase in the case of calcium phosphate; an increase in the amount of calcium in solution in the last case undoubtedly occurs.

The acidity of pure aqueous solutions of the phosphates seems to be roughly proportional to the quantity of phosphoric acid found in the solution, but in presence of soluble salts a connection between the acidity and the dissolved phosphoric acid cannot be recognised. Thus, sodium nitrate, potassium chloride, and potassium sulphate all increase the acidity of solutions in contact with ferric phosphate, whilst the first two of these salts decrease the amount of the dissolved phosphoric acid. No connection can be traced between the acidity and the amount of iron in solution, although the quantity of base in solution is increased. In the case of calcium phosphate, potassium chloride and sodium nitrate decrease the acidity instead of increasing it, as with ferric phosphate; in both cases, however, the quantity of calcium in solution decidedly increases, and, in the case of sodium nitrate, the

phosphoric acid increases also. In all the experiments which were made to ascertain the influence of temperature, a rise in temperature increased the proportion of decomposition of the phosphate both with aqueous and saline solutions.

W. A. D.

Action of Chloric Acid on Metals. WALTER S. HENDRIXSON (*J. Amer. Chem. Soc.*, 1904, 26, 747—758).—The chloric acid used by the author could be heated to 95° without undergoing any considerable amount of decomposition.

Sodium and potassium amalgam have a slight reducing action on chloric acid. With magnesium, about 1/20th of the amount used acted in reducing the chloric acid, the remainder dissolving to form the chlorate with the evolution of an approximately equivalent quantity of hydrogen. With chloric acid of 2*N*-strength, the amount of hydrogen set free by its action on zinc is much smaller than when *N*-chloric acid is used, whilst the amount of acid reduced is correspondingly greater.

The amount of hydrogen evolved by the action of 2*N*-chloric acid on aluminium was measured; the aluminium was completely dissolved. Iron dissolves readily in dilute or strong chloric acid without evolution of hydrogen or any other gas, the acid being very readily reduced. No hydrogen is evolved by the action of tin on chloric acid; the tin is dissolved by the acid. The behaviour of copper and of cadmium is similar to that of tin, no hydrogen being evolved in either case. Mercury and antimony are attacked very slowly; nickel dissolves readily, whilst the action on bismuth is slow. Arsenic dissolves to form arsenic acid.

Bromic acid acts on silver according to the equation: $6\text{Ag} + 6\text{HBrO}_3 = 5\text{AgBrO}_3 + \text{AgBr} + 3\text{H}_2\text{O}$ (compare Hendrixson, *Abstr.*, 1903, ii, 596).

A. McK.

Action of Ammonium Chloride on Certain Chlorides. I. Action on Metallic Chlorides. PETER FIREMAN (*J. Amer. Chem. Soc.*, 1904, 26, 741—747).—When antimony pentachloride is heated with ammonium chloride at 380—410°, the reaction is represented by the equation $3\text{SbCl}_5 + 2\text{NH}_4\text{Cl} = 3\text{SbCl}_3 + 8\text{HCl} + \text{N}_2$. When ammonium chloride is heated with titanium tetrachloride at 260—410°, scarcely any gaseous products are evolved, but a greenish-yellow, solid double salt is formed. The reaction between ferric chloride and ammonium chloride, at 400—420°, probably takes place according to the equation $3\text{FeCl}_3 + \text{NH}_4\text{Cl} = 3\text{FeCl}_2 + 4\text{HCl} + \text{N}$, since the amount of gas evolved is in agreement with the action thus represented. Similarly, the amount of gas evolved when cupric chloride is heated with ammonium chloride indicates that the reaction is represented as follows: $3\text{CuCl}_2 + \text{NH}_4\text{Cl} = 3\text{CuCl} + 4\text{HCl} + \text{N}$. No gas is evolved when ammonium chloride is heated with mercuric chloride, a double salt being produced in this case.

Only those metallic chlorides which dissociate more or less readily are reduced to a lower degree of chlorination when heated in a closed tube with ammonium chloride, the latter breaking up completely with elimination of nitrogen.

A. McK.

Mutual Rearrangement in Molten Masses of Mixtures of Halogen Salts. NICOLAI N. BÉKÉTOFF [with WL. BÉKÉTOFF] (*Zeit. anorg. Chem.*, 1904, 40, 355—371).—In 1859, the author formulated the rule: elements of the same valency distribute themselves in such a manner that positive elements with high atomic weights combine preferentially with negative elements with high atomic weights, whilst positive elements with small atomic weights combine with negative elements with small atomic weights. For example, in the interaction between lithium, caesium, chlorine, and iodine, with the atomic weights 7, 133, 35·5, and 127 respectively, lithium chloride and caesium iodide are the main products, since the value $(127 \times 133) + (35 \cdot 5 \times 7)$ is greater than the value $(127 \times 7) + (35 \cdot 5 \times 133)$. The author's views have since been confirmed by Gustavson and Potylizyn in their experiments on the displacement of a halogen element from its salts by means of another halogen.

The author has now examined the heat of solution of a mixture of two alkali haloids, for example, the heat of solution of a mixture of sodium chloride and potassium iodide was first determined, then that of a mixture of sodium iodide and potassium chloride, and, finally, that of the molten mass. When the heat of solution of the individual salt pairs is known, the amount of interchange in the molten mass can be calculated from its observed heat of solution. The fusion of a pure salt does not cause an alteration in its molecular structure of such a nature that the heat of solution is influenced. There was no probability of the formation of double salts in the cases examined. The behaviour of all the possible combinations of lithium, sodium, potassium, and caesium respectively with chlorine and with iodine was experimentally investigated, and the results found to accord with the author's rule.

A. McK.

Sodium Amalgams. A. SCHULLER (*Zeit. anorg. Chem.*, 1904, 40, 385—399).—The composition of various sodium amalgams was investigated by the author according to Tammann's method (this vol., ii, 113). A weighed quantity of sodium was heated to its melting point and a weighed amount of mercury added. The curves of cooling were determined by mercury in alcohol thermometers, and in some cases by a thermo-element. The various curves are given, the ordinates representing temperatures and the abscissæ concentrations. The times within which the temperatures remained constant are represented by vertical lines, the lengths of which are proportional to the times. The values agree on the whole with Kurnakoff's results, although the temperatures are in most cases higher. The curve exhibits breaks at the following temperatures: $-38 \cdot 6^\circ$, $-48 \cdot 2^\circ$, 159° , 360° , 227° , 219° , 123° , $66 \cdot 2^\circ$, $33 \cdot 9^\circ$, $21 \cdot 4^\circ$, and $97 \cdot 5^\circ$, corresponding with the following atomic percentages of mercury, 100·0, 2·8 [197·2], 81·9, 66·7, 51·9, 49·1, 38·1, 28·2, 15·9, 14·8, 0·0 respectively. The compound NaHg_2 exists at 360° , the maximum of the melting point curve, but when mercury is added to this substance, the melting point is lowered, until, at 159° , the compound NaHg_4 crystallises. At atomic concentrations of mercury between 97° and 100° , only mercury separates. At 227° , where the atomic concentration of mercury is about 52, the compound $\text{Na}_{12}\text{Hg}_{13}$

is probably formed. When the atomic concentration of mercury is 50, the compound NaHg separates. When the concentration of sodium is further increased, crystals of the compound Na_3Hg_2 separate from the liquid amalgam. When the temperature sinks to 66.2° , a conglomerate of Na_3Hg_2 and Na_5Hg_2 is produced. At 33.9° , the compound Na_3Hg is formed, whilst at 21.4° a eutectic mixture of Na_3Hg and sodium results. At 97.5° , pure sodium separates.

The preparation of the various amalgams is described. A. McK.

Solubility of Potassium and Barium Nitrates and Chlorides.

HARRY W. FOOTE (*Amer. Chem. J.*, 1904, 32, 251—253).—The solubility relations of the double salt, $2\text{KNO}_3 \cdot \text{Ba}(\text{NO}_3)_2$ (Wallbridge, *Abstr.*, 1903, ii, 646), have been studied at 25° by means of the method previously described (*Abstr.*, 1903, i, 797). The double salt is stable over a wide range of composition of the solution. Potassium and barium chlorides do not form a double salt at 25° . C. H. D.

Silver Dihydrogen Pyrophosphate. JACQUES CAVALIER (*Compt. rend.*, 1904, 139, 284—286).—Silver dihydrogen pyrophosphate, obtained by heating a mixture of silver pyrophosphate and pyrophosphoric acid until the liquid is clear, dissolving in a small quantity of water at 0° , and precipitating with alcohol or ether, is a white, crystalline powder, which softens at 150° and melts and decomposes at 240° when heated gradually, whilst the melting point, as determined by Maquenne's metal block process, is 235° . It is decomposed by cold water, yielding the normal salt and pyrophosphoric acid; it reacts with sodium orthophosphate to form silver orthophosphate and pyrophosphoric acid, and with alkyl iodides to form silver iodide and the alkyl esters of pyrophosphoric acid.

M. A. W.

Solubility of Barium and Mercuric Chlorides.

HARRY W. FOOTE and HOWARD S. BRISTOL (*Amer. Chem. J.*, 1904, 32, 246—251).—The existence of a double salt of barium and mercuric chlorides was sought for by means of the solubility method previously described (*Abstr.*, 1903, i, 797; ii, 728). No double salt was found to exist at 25° . Dilatometric experiments indicated a transition-point at 17.2° . Below this temperature, the salt $\text{BaCl}_2 \cdot 3\text{HgCl}_2 \cdot 6\text{H}_2\text{O}$ forms, and was detected by the solubility method at 10.4° . Bonsdorf's salt, $\text{BaCl}_2 \cdot 2\text{HgCl}_2 \cdot 2\text{H}_2\text{O}$ (1829), is not formed under the conditions given by him. C. H. D.

Revision of the Atomic Weight of Glucinum. CHARLES LATHROP PARSONS (*J. Amer. Chem. Soc.*, 1904, 26, 721—740).—The atomic weight of glucinum had hitherto been determined by Nilson and Petterson and others from analyses of the hydrated sulphate, $\text{GISO}_4 \cdot 4\text{H}_2\text{O}$, the only other method used being that of Debray, who analysed the double oxalate, $\text{Gl}(\text{NH}_4)_2(\text{C}_2\text{O}_4)_2$.

The purification of beryl and of Kahlbaum's hydroxide is first described. A basic carbonate of the approximate composition $\text{GlCO}_3 \cdot [\text{Gl}(\text{OH})_2]_3 \cdot 2\text{H}_2\text{O}$ was obtained, which served as a basis for the production of purer salts used in the atomic weight determina-

tions of the author. Kahlbaum's hydroxide contains aluminium and iron along with traces of zinc. Analysis of glucinum chloride is unsuitable for the determination of the atomic weight, owing to the great ease with which it is acted on by water and to the fact that it attacks glass. The author was unable to obtain the compound $\text{GlCl}_2 \cdot 4\text{H}_2\text{O}$, described by Awdejew.

Atomic weight determinations, based on analyses of the hydrated sulphate, $\text{GlSO}_4 \cdot 4\text{H}_2\text{O}$, gave values varying from 9.18 to 9.36, but are regarded by the author as unsatisfactory, as the specimens of the hydrated sulphate examined tend to vary in composition owing to the ease with which the water of crystallisation is lost at comparatively low temperatures.

The preparation of pure glucinum acetylacetonate is described. The atomic weight of glucinum was determined by heating the acetylacetonate, first at 50° for 24—48 hours with pure redistilled nitric acid, then for 48 hours at 100° , and, finally, for several hours at 175° . The complete conversion of the nitrate into oxide was finally effected at a bright red heat. The value, obtained in this manner, as a mean of seven determinations, was 9.113 ± 0.0059 ($O = 16$).

The atomic weight was also determined by the conversion of the basic acetate, $\text{Gl}_2\text{O}(\text{C}_2\text{H}_3\text{O}_2)_6$, into the oxide, the method being almost identical with that employed for the acetylacetonate. The value 9.113 ± 0.0033 ($O = 16$) was obtained as a mean of nine determinations.

The atomic weight of glucinum, deduced from these two methods, is accordingly 9.113 ± 0.0043 ($O = 16$).
A. McK.

Glucinum Compounds. II. Preparation of Pure Glucinum Hydroxide. FRITZ HABER and G. VAN OORDT (*Zeit. anorg. Chem.*, 1904, 40, 465—468. Compare this vol., ii, 257).—Glucinum hydroxide may be separated from aluminium oxide and ferric hydroxide by means of glacial acetic acid; which forms a basic glucinum acetate, very readily soluble in chloroform, from the solution in which it is not extracted by water. Aluminium oxide and iron hydroxide also form compounds with glacial acetic acid, which do not, however, dissolve in chloroform. When the basic glucinum acetate is dissolved in warm acetone and a cold aqueous solution of sodium carbonate then added, glucinum hydroxide is precipitated.
A. McK.

Zinc and Cadmium Chromates. MAX GRÖGER (*Monatsh.*, 1904, 25, 520—536. Compare Abstr., 1903, ii, 647).—The action of an excess of zinc chloride on potassium chromate in aqueous solution (N or $3N$) leads to the formation of a yellow, granular precipitate, which has the composition $4\text{ZnO} \cdot \text{K}_2\text{O} \cdot 4\text{CrO}_3 \cdot 3\text{H}_2\text{O}$. By repeated treatment with hot water, this is converted into the insoluble basic zinc chromate, $\text{ZnCrO}_4 \cdot 3\text{Zn}(\text{OH})_2$, which is a dark yellow powder. When fused, the zinc potassium chromate evolves oxygen, the residue consisting of potassium chromate and insoluble violet zinc chromite, $8\text{ZnO} \cdot 3\text{Cr}_2\text{O}_3$.

The proportion of potassium, and, to a less extent, that of chromium, is increased by the use of excess of the potassium chromate; with normal solutions, the precipitate has the molecular composition, ZnO ,

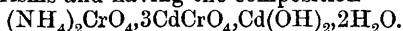
0.394 K_2O , 1.094 CrO_3 ; with 3*N* solutions, ZnO , 0.486 K_2O , 1.222 CrO_3 . When treated with hot water, these precipitates yield the foregoing basic zinc chromate. These precipitates are of a deeper yellow than that formed in presence of excess of zinc salt, but after prolonged contact (2 weeks) with the mother liquor they assume the colour and composition of the latter.

The action of zinc chloride on sodium chromate leads to the formation of basic zinc chromate, $ZnCrO_4 \cdot 3Zn(OH)_2$, which is obtained as a horny mass.

Ammonium chromate and excess of zinc chloride give rise to a dark yellow, granular precipitate, ZnO , 0.279 $(NH_4)_2O$, 0.822 CrO_3 , which is possibly a mixture, and is decomposed by cold water. The orange-yellow precipitate, formed by the action of an excess of ammonium chromate on zinc chloride, is stable to water or its mother liquor and has the composition $(NH_4)_2CrO_4 \cdot ZnCrO_4 \cdot Zn(OH)_2$. When strongly heated, it decomposes suddenly, evolving nitrogen and water vapour; the residue is a powder consisting of zinc oxide and chromite, $2ZnO \cdot Cr_2O_3$.

On mixing aqueous solutions of potassium chromate and pure cadmium chloride, a canary-yellow, granular precipitate is formed having the composition $K_2CrO_4 \cdot 3CdCrO_4 \cdot Cd(OH)_2 \cdot 2H_2O$. Contrary to Preis and Raymann's statement (*Abstr.*, 1880, 444), this same precipitate is formed by the action of cadmium sulphate and potassium chromate. Cadmium potassium chromate is more stable to boiling water than is zinc potassium chromate, but is finally converted into a lemon-yellow powder, 84.53 per cent. of which is cadmium chromite.

On mixing aqueous solutions of cadmium chloride and sodium chromate, a yellow, flocculent precipitate is formed which rapidly becomes granular; it is a basic cadmium chromate which easily loses chromic acid when washed with water and absorbs carbon dioxide when exposed to air. When equal volumes of cadmium chloride and sodium chromate solutions are mixed hot and boiled for three days, during which period the precipitate formed is washed twenty-four times, the residue obtained has the molecular proportion CdO , 0.342 CrO_3 , 1.428 H_2O . Cadmium chloride and ammonium chromate interact in aqueous solution, forming a dark yellow precipitate consisting of microscopic prisms and having the composition



The action of hot water on the precipitate leads finally to basic cadmium chromate. When heated, cadmium ammonium chromate leaves a green residue containing cadmium and chromic oxide.

G. Y.

Dissociation of Lead Nitrate. J. LIVINGSTONE R. MORGAN (*J. Physical Chem.*, 1904, 8, 416—420).—In the dissociation of lead nitrate according to the equation $Pb(NO_3)_2 \rightleftharpoons PbO + \frac{1}{2}O_2 + 2NO_2$, at any temperature, the value $\sqrt{p_1 \cdot p_2^2}$ should be constant; $p_1 p_2$ being the pressures of oxygen and nitric peroxide. From the values obtained by Baekeland for the pressure of lead nitrate at various temperatures, alone and in the presence of excess of nitric peroxide or oxygen, data are obtained to test this constancy. The values so obtained for the constant are

(1) alone, 0.062; (2) in excess of nitric peroxide, 0.098; (3) in excess of oxygen, 0.011 and 0.0091. The author considers that these indicate that the reaction proceeds according to the equation in the first two cases, but that excess of oxygen causes a different action, probably owing to the formation of a basic salt. The heat of dissociation calculated from the vapour pressure is found to agree with the heat of formation calculated from thermochemical data. L. M. J.

The Form in which Thallous Iodide separates from Solution. DESIRÉ GERNEZ (*Compt. rend.*, 1904, 139, 278—281. Compare this vol., ii, 617).—When aqueous solutions of yellow thallous iodide are allowed to cool slowly in the presence of some of the undissolved solid, crystals of the yellow variety, the stable form below 168°, are deposited; if, however, the hot solution is filtered, or cooled rapidly, crystals of the red or unstable form are obtained. Thallous iodide is very sparingly soluble in water, one part dissolving in 16,000 parts of water at 16°, and being even less soluble in alcohol or the other organic solvents; it is, however, more readily soluble in saturated saline solutions, and from such solutions, either filtered or containing excess of the undissolved yellow iodide, the unstable red variety is deposited on cooling, and its conversion into the stable yellow variety is extremely slow, lasting over a period of two years. As regards the deposition of the unstable variety from solutions, thallous iodide resembles mercuric iodide (compare Abstr., 1903, ii, 481).

M. A. W.

Constitution of Hydrated Thallic Chloride. F. M. McCLENAHAN (*Amer. J. Sci.*, 1904, [iv], 18, 104—112).—From the way in which tetrahydrated thallic chloride loses its water in dry air, the formula may be written $\text{TiCl}_3 \cdot \text{H}_2\text{O} \cdot \text{H}_2\text{O} \cdot 2\text{H}_2\text{O}$. At 100°, practically all the water is lost in an hour, and there is very little loss of chlorine. When the salt is heated in hydrogen chloride at varying temperatures up to 100°, the sequence of changes is represented by the following formulæ: $\text{TiCl}_3 \cdot \text{H}_2\text{O} \cdot \text{H}_2\text{O} \cdot 2\text{H}_2\text{O}$; $\text{TiCl}_3 \cdot \text{H}_2\text{O} \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$; $\text{TiCl}_3 \cdot \text{H}_2\text{O}$; TiCl_3 . A structural formula is written for the hydrated salt in accordance with Cushman's hypothesis of quadrivalent oxygen (Abstr., 1902, ii, 322).

L. J. S.

Crystallised Copper Iodates. A. GRANGER and AUGUST DE SCHULTEN (*Compt. rend.*, 1904, 139, 201—203).—When a dilute solution of potassium iodate is added drop by drop to a very faintly acid solution of copper sulphate heated on the water-bath, dark green, orthorhombic crystals of the basic iodate, $\text{CuIO}_3 \cdot \text{OH}$, separate. The crystals (sp. gr. 4.878 at 15°) can be heated to 290° without change; at higher temperatures, water, iodine vapour, and oxygen are evolved. Blue, triclinic crystals of the normal iodate, $\text{Cu}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$ (sp. gr. 4.876 at 15°), separate when the dilute potassium iodate solution is slowly added to a hot copper nitrate solution containing a considerable quantity of nitric acid. When the hydrated normal iodate is distilled on the water-bath with nitric acid of sp. gr. 1.33, pale green, mono-

clinic crystals of the anhydrous salt, $\text{Cu}(\text{IO}_3)_2$ (sp. gr. 5.241 at 15°), are deposited. Addition of potassium iodate solution to the solution of a copper salt containing more than a very small quantity of free acid leads to the formation of both the normal iodate and the basic iodate. Crystallographic measurements of the three salts are recorded.

H. M. D.

Cuprammonium Sulphates. DAVID W. HORN and EDYTHA E. TAYLOR (*Amer. Chem. J.*, 1904, 32, 253—285).—Berzelius' cuprammonium sulphate, $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$, is best prepared by Andrae's method of passing ammonia gas into a solution of copper sulphate and drying over lime. It is stable in dry air, but loses ammonia when moist. On heating at various temperatures, only mixtures containing basic salts are obtained. The salt forms a clear solution in water, but on dilution to 1/20th or 1/25th normal, a permanent precipitate is produced.

C. H. D.

Constitution of Copper Zinc Alloys. E. S. SHEPHERD (*J. Physical Chem.*, 1904, 8, 421—435).—The author finds that no definite compounds of copper and zinc can exist, but that six different solid phases occur which are all solid solutions. The composition of the solids which can be in equilibrium with different fusions is given, and also the percentage of copper in the crystals at 400° . The latter are: α , 64—100; β , 51—53.5; γ , 31—40; δ , unstable at 400° ; ϵ , 13—19; η , 0—2.5. The α -crystals vary in colour from yellow to copper-red, the β -crystals are red, and this explains the red colour of brasses containing 40 to 60 per cent. of copper. The micro-structure of the brasses is also considered, and the paper is illustrated by 46 photomicrographs, which show the crystalline structure as well as the effects of heat and annealing on the different alloys.

L. M. J.

Some Cerium Compounds. JEAN STERBA (*Ann. Chim. Phys.*, 1904, [viii], 2, 193—232).—This paper is largely a résumé of work already published (compare Abstr., 1901, ii, 602; 1902, ii, 399, 563). Pure cerium sulphide, Ce_2S_3 , prepared by the action of hydrogen sulphide on cerium oxide, hydroxide, sulphate, or carbonate at a red heat, does not ignite spontaneously (compare Muthmann and Stützell, Abstr., 1900, ii, 142), but an oxysulphide obtained by the action of moist hydrogen sulphide has this property. Mosander's golden-yellow crystalline cerium sulphide (compare Muthmann and Stützell, Abstr., 1900, ii, 142) is crystallised ferric sulphide.

M. A. W.

Chromate, Dichromate, and Chromic Acid. RICHARD ABEGG and A. J. COX (*Zeit. physikal. Chem.*, 1904, 48, 725—734).—The addition of soluble barium or silver salts to a solution of a dichromate results in the precipitation of sparingly soluble normal chromates, hence a dichromate solution must contain normal chromate and free chromic acid. The equilibrium may be represented by the equation $\text{Cr}_2\text{O}_7'' \rightleftharpoons \text{CrO}_4'' + \text{CrO}_3$, and various ways of determining the constant $K = [\text{Cr}_2\text{O}_7'']/[\text{CrO}_4''] \cdot [\text{CrO}_3]$ are discussed. The knowledge of the solubility product for some of the sparingly soluble normal chromates

would furnish one method of evaluating K , but sufficient data are not available. One of the authors (C.) has found that normal mercuric chromate is hydrolysed into a sparingly soluble basic salt, $\text{HgCrO}_4 \cdot 2\text{HgO}$, and free chromic acid, which accumulates in the solution until its molecular concentration is 0.706 at 50° and 0.456 at 25° . Thus, using a mixture of normal and basic chromate as a regulator for the concentration of free chromic acid, the authors have found $K=0.96$ at 50° and $=1.08$ at 25° . This means that (1) a dichromate solution contains a relatively small quantity of $\text{Cr}_2\text{O}_7^{''}$ ions, a result borne out also by freezing point experiments; (2) as the temperature rises, the quantity of $\text{Cr}_2\text{O}_7^{''}$ ions diminishes in favour of normal chromate ions and chromic acid. Chromic acid itself is to be regarded as a weak acid, the salts of which are hydrolysed in the usual manner.

J. C. P.

Action of Zinc on the Sodium Tungstates. L. A. HALLOPEAU (*Compt. rend.*, 1904, 139, 283—284. Compare Abstr., 1900, ii, 8).—Delépine (compare Abstr., 1900, ii, 548) has shown that tungsten trioxide or ammonium tungstate is readily reduced by zinc, but the author finds that zinc at its boiling point has no action on sodium tungstate, $\text{Na}_2\text{O} \cdot \text{WO}_3 \cdot 2\text{H}_2\text{O}$, whilst under the same conditions sodium paratungstate, $5\text{Na}_2\text{O} \cdot 12\text{WO}_3 \cdot 28\text{H}_2\text{O}$, yields zinc tungstate, $\text{ZnO} \cdot \text{WO}_3$, in the form of large, prismatic crystals, a small quantity of Wöhler's sodium tungsto-tungstate, $\text{Na}_2\text{O} \cdot \text{WO}_3 \cdot \text{WO}_2 \cdot \text{WO}_3$, in the form of golden-yellow scales, and traces of tungsten in the form of a grey, amorphous powder.

M. A. W.

Separation of Thorium from Cerium, Lanthanum, and Didymium by *m*-Nitrobenzoic Acid. ARTHUR C. NEISH (*J. Amer. Chem. Soc.*, 1904, 26, 780—793).—*m*-Nitrobenzoic acid precipitates thorium quantitatively as $\text{Th}(\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2)_4$ from a neutral solution of the nitrate. When this precipitation is repeated, it affords a complete separation from cerium, lanthanum, and didymium. This method gives as good results for thorium in monazite as the combination or fumaric acid methods; it is much shorter and offers no difficulties in precipitation or filtration; moreover, with this precipitant, the use of alcohol is avoided.

A. McK.

Thorium, Carolinium, Berzelium. CHARLES BASKERVILLE (*J. Amer. Chem. Soc.*, 1904, 26, 922—941. Compare Abstr., 1902, ii, 85).—Attempts to fractionate thorium compounds with phenylhydrazine according to Jefferson's method (Abstr., 1902, ii, 534) having proved unsatisfactory, pure thorium oxide was heated with sugar carbon in quartz tubes in a current of chlorine. A white vapour first distilled which was partly condensed in the cooler portion of the tube and partly absorbed by alcohol; by dissolving this chloride in water, digesting the resulting oxide with hydrofluoric, hydrochloric, and nitric acids, subsequently dissolving in hot sulphuric acid (1:1), precipitating with ammonia, and igniting, a slightly green oxide was obtained having a sp. gr. 8.47 and belonging to an element, *berzelium*, with an atomic weight 212. This oxide was only very slightly radioactive. The thorium chloride, which subsequently sublimed in crystals, after puri-

fication similar to that described above, gave the values 220.1—220.6 for the atomic weight of thorium, very much lower than that usually accepted for the metal. The non-volatile residual chloride remaining after the removal of thorium and berzelium gave an *oxide* which was soluble in concentrated hydrochloric acid; the *chloride* so formed crystallised from the acid, and belonged to a metal, *carolinium*, with an atomic weight of 255.6. Carolinium oxide has a sp. gr. 11.26, that of thorium oxide being 10.53.

The ultra-violet spectra of the new substances, when examined by Sir William Crookes between $\lambda 3444$ and 4071.9 , showed prominent lines identical with those of thorium.

W. A. D.

Further Experiments with Vanadium Steels. LÉON GUILLET (*Compt. rend.*, 1904, 139, 407—409. Compare this vol., ii, 266).—Vanadium steels are sensitive to thermal treatment, and annealing brings about considerable changes in the mechanical properties. After being heated at 900° and slowly cooled, vanadium steels exhibiting perlite structure are not more fragile than ordinary steels containing the same amount of carbon. Steels containing a large proportion of vanadium, in which all the carbon is present in the form of carbide are quite heterogeneous.

H. M. D.

Platinum Oxides. LOTHAR WÖHLER [and, in part, with A. VON DIETERICH and F. STRUBE] (*Zeit. anorg. Chem.*, 1904, 40, 423—464. Compare this vol., ii, 44).—Only two oxides of platinum exist, namely, the peroxide, PtO_2 , which forms several hydroxides, exhibiting different colours, and the suboxide, PtO , which also forms hydroxides. Since the platinum hydroxides readily form colloidal solutions, are very slightly basic, and, on precipitation, retain foreign substances, the various other oxidation products of platinum, previously described by other authors, are supposed not to exist. The analytical methods previously employed are also not free from objection.

In the author's experiments, the analyses of the oxides were conducted by estimating the oxygen volumetrically; the oxide is heated to redness in a current of carbon dioxide, the gases being collected over potassium hydroxide and measured. The water was determined by heating the oxide in a current of dry air and passing the products through a weighed calcium chloride tube. The hydroxides retain water in a remarkable manner, for example, the platinous hydroxide still retains 8.4 per cent. of its water when heated for 14 days at 300° , an amount which diminishes to 6.6 per cent. when the heating is continued for 16 days longer at 405° , the theoretical amount of water in $\text{Pt}(\text{OH})_2$ being 7.9. The behaviour of platinic hydroxide is similar. The partially-dehydrated hydroxides exhibit a much smaller solubility in dilute mineral acids than do the freshly-precipitated hydroxides. Platinic oxide, being more acidic than basic, is termed "platinic acid." Its salts undergo considerable hydrolytic dissociation. Platinous oxide is fully acidic.

Platinic hydroxide is prepared as follows: platinic chloride is boiled with an excess of 2*N*-sodium hydroxide, the solution cooled, and then neutralised with acetic acid, when the hydroxide, $\text{H}_2\text{Pt}(\text{OH})_6$, is pre-

precipitated as a yellow powder. When the latter is heated, it turns brown and then black. When the precipitated hydroxide is boiled for a long time, it is converted into the compound $\text{PtO}_2 \cdot 3\text{H}_2\text{O}$, which, when left over sulphuric acid in a desiccator, is converted into the compound $\text{PtO}_2 \cdot 2\text{H}_2\text{O}$. The latter hydroxide, when heated at 100° , becomes dark coloured, with the formation of the compound $\text{PtO}_2 \cdot \text{H}_2\text{O}$, which parts with its water with great difficulty. The monohydrate is insoluble in aqua regia and in hydrochloric acid. The platinum tetroxide, described by Jørgensen, does not exist. Illustrations are given of the oxidising action of the dioxide. Platinic hydroxide undergoes appreciable decomposition into platinous oxide when heated at 300° in a current of carbon dioxide. Anhydrous platinous oxide is probably stable in the presence of oxygen at 510° .

When potassium platinous chloride is boiled with the calculated amount of aqueous sodium hydroxide solution, a dark precipitate of platinous hydroxide is formed. It cannot be completely dehydrated. Platinous oxide appears to be a stronger oxidising agent than the dioxide, and a better reducing agent than platinum itself.

A. McK.

Ruthenium. VI. The Bromides. JAMES L. HOWE (*J. Amer. Chem. Soc.*, 1904, 26, 942—946).—*Potassium ruthenobromide*, K_2RuBr_5 , obtained by adding potassium bromide to a solution of ruthenium tetroxide in hydrobromic acid and evaporating over sulphuric acid, forms small, brown crystals and is decomposed by water; as the same salt is obtained by adding potassium chloride to a concentrated solution of ruthenobromous acid, the latter probably exists in solution as H_2RuBr_5 and not as $\text{RuBr}_3 \cdot 2\text{HBr}$. *Rubidium ruthenobromide*, $\text{Rb}_2\text{RuBr}_5 \cdot \text{H}_2\text{O}$, obtained in the same way by using rubidium bromide, crystallises from dilute hydrobromic acid. *Cesium ruthenobromide*, $\text{Cs}_2\text{RuBr}_5 \cdot \text{H}_2\text{O}$, forms slender, black needles.

Potassium aquoruthenibromide, $\text{K}_2\text{Ru}(\text{H}_2\text{O})\text{Br}_5$, prepared by boiling potassium ruthenobromide with alcohol and hydrobromic acid and evaporating the solution, separates in minute, brown crystals. The analogous *rubidium aquoruthenibromide* forms a brownish-black, crystalline mass.

Potassium ruthenibromide, K_2RuBr_6 , obtained by passing bromine vapour through a concentrated solution of the aquoruthenibromide at 0° , crystallises in minute, black octahedra. *Rubidium ruthenibromide* is similar, but less soluble.

W. A. D.

Preparation and Properties of Ruthenium Silicide. HENRI MOISSAN and WILHELM MANCHOT (*Ann. Chim. Phys.*, 1904, [viii], 2, 285—288).—A résumé of work already published (compare Abstr., 1903, ii, 604).

M. A. W.

Mineralogical Chemistry.

Ratio of Radium to Uranium in Some Minerals. BERTRAM B. BOLTWOOD (*Amer. J. Sci.*, 1904, [iv], 18, 97—103).—Various uranium minerals (uraninite, gummite, uranophane, samarskite, and carnotite) were heated with acid, and the radium emanation transferred to a specially constructed, air-tight, gold-leaf electroscope, the rate of discharge of which was taken to indicate the proportion of radium in the mineral. It was found that the amount of radium in each mineral is directly proportional to the amount of uranium. This affords experimental evidence in favour of the suggestion that radium is formed by the breaking down of the uranium atom. L. J. S.

An Occurrence of Native Iron. JAKOB BECKENKAMP (*Sitz.-Ber. Physikal.-med. Ges. Würzburg*, 1904, 59—65).—A spring-boring at Dettelbach, near Würzburg, after passing through three metres of solid rock, entered beds of grey and red clay of Keuper age; in the latter was found metallic iron as minute particles and pieces up to 30 grams in weight. The iron is of two kinds, with the characters of cast iron and wrought iron respectively. Darker-coloured fragments have sp. gr. 7·0—7·1, and Fe 95, C 5 per cent.; the lighter-coloured have sp. gr. 7·6—7·8, and Fe 99·8, C 0·02. Some of the fragments have a thin, yellow coating, which has the appearance and composition of brass. The characters of this metallic iron are not those of meteoric iron, and it is possible that it is of artificial origin, and may have been thrown into the spring to improve the water. L. J. S.

Analyses of Lorandite and Claudetite. JOSEF LOCZKA (*Zeit. Kryst. Min.*, 1904, 39, 520—525).—A new analysis of lorandite from Macedonia (Abstr., 1896, ii, 30; this vol., ii, 416) gave: Ti, 59·76; As, 22·30; S, 18·99 per cent. Formula, TiAsS_2 . Sp. gr. 5·53.

An analysis of claudetite, the monoclinic modification of arsenic trioxide, from Szomolnok, Hungary, gave: As, 75·99 (calc. for As_2O_3 , 75·78); insoluble residue, 0·17. L. J. S.

Axial Ratios and Chemical Composition of Ilmenite. G. DOBY and G. MELCZER (*Zeit. Kryst. Min.*, 1904, 39, 526—540).—Crystallographic descriptions are given of ilmenite from various localities, and the following analyses were made of the crystals which were measured. The results for the material from Prägraten are quoted from Sustschinsky (Abstr., 1903, ii, 84).

| Locality. | Axial ratio, $a:c$. | Sp. gr. | TiO_2 . | FeO. | Fe_2O_3 . | CaO. | MgO. | Total. |
|------------------|-------------------------|---------|------------------|-------|---------------------------|------|------|----------|
| Snarum..... | 1:1·368 | 5·041 | 5·66 | 0·11 | 93·50 | — | 1·10 | 100·37 * |
| Tvedestrand..... | 1:1·3716 | 4·910 | 21·58 | 8·04 | 70·39 | — | — | 100·01 |
| Ilmen Mtns. ... | 1:1·3772 | 4·852 | 47·68 | 19·70 | 33·90 | — | 0·35 | 101·63 |
| Kragerö..... | 1:1·379 | 4·614 | 49·68 | 15·72 | 34·51 | 0·07 | — | 99·98 |

Prägraten 1:1·3844 — 57·23 40·31 1·15 1·22 100·76 †

* Also trace Mn_2O_4 .

† Including: Al_2O_3 , 0·74; Mn_2O_4 , 0·11.

These results show that with increase in titanitic acid the vertical (c) axis becomes longer and the specific gravity less. L. J. S.

Minerals [allied to Pyrochlore and Euxenite] from Batum, Caucasus. G. P. TSCHERNIK (*Zeit. Kryst. Min.*, 1904, 39, 624—625; from *Ann. Géol. Min. Russ.*, 1902, 5, 196—203).—Embedded in the felspar of a granite boulder from the bed of the Tschoroch river in the province of Batum were reddish-brown, octahedral crystals of a mineral with the characters of pyrochlore; its composition is given under I. In the same boulder was a vein of a black mineral with the composition given under II; this mineral has a certain resemblance to euxenite, although it is distinct from this.

| | Ch ₂ O ₅ . | Ta ₂ O ₅ . | ThO ₂ . | TiO ₂ . | SiO ₂ . | Ce ₂ O ₃ . | La ₂ O ₃ . | Di ₂ O ₃ . | Y ₂ O ₃ + Er ₂ O ₃ . | UO ₂ . |
|-----|----------------------------------|----------------------------------|--------------------|--------------------|--------------------|----------------------------------|----------------------------------|----------------------------------|--|-------------------|
| I. | 26.22 | 27.39 | trace | 4.20 | — | 12.34 | 0.71 | 0.63 | — | 8.33 |
| II. | 22.20 | — | trace | 33.31 | 7.03 | 8.53 | 0.55 | 0.48 | 11.20 | 11.11 |
| | Fe ₂ O ₃ . | FeO. | CaO. | MnO. | MgO. | Na ₂ O. | H ₂ O. | F. | Total. | Sp. gr. |
| I. | 0.26 | 6.32 | 6.00 | trace | trace | 3.15 | 1.45 | 1.90 | 98.90 | 4.21 |
| II. | 3.24 | — | 0.44 | — | — | — | 0.93 | — | 99.02 | 4.975 |

L. J. S.

Fergusonite from the Caucasus. G. P. TSCHERNIK (*Zeit. Kryst. Min.*, 1904, 39, 625; from *Ann. Géol. Min. Russ.*, 1902, 5, 221).—Embedded in the quartz of a fragment of granite from the bed of the Terek river were small, black crystals, which appeared to have the form of a tetragonal pyramid; the following analysis proves the mineral to be fergusonite, which has not previously been recorded from Russia.

| Ch ₂ O ₅ + Ta ₂ O ₅ . | Y ₂ O ₃ + Er ₂ O ₃ . | Ce ₂ O ₃ . | La ₂ O ₃ . | Di ₂ O ₃ . | ZrO ₂ . | FeO. | UO ₂ . | WO ₃ . |
|---|--|----------------------------------|----------------------------------|----------------------------------|--------------------|---------|-------------------|-------------------|
| 42.71 | 36.52 | 3.65 | 0.25 | 0.20 | 1.06 | 1.22 | 6.33 | 0.69 |
| SnO ₂ . | CaO. | MnO. | H ₂ O. | Loss on ignition. | Total. | Sp. gr. | | |
| 0.12 | 2.34 | 0.52 | 3.09 | 0.32 | 99.62 | 5.657 | | |

L. J. S.

Muscovite from Kossoj-Brod, Urals. L. IWANOFF (*Zeit. Kryst. Min.*, 1904, 39, 623; from *Bull. Soc. Imp. Natur. Moscou*, 1902, 16, 507—510).—A “refractory clay” from Kossoj-Brod, in the Sysstert district, consists of quartz sand and scales of muscovite. The muscovite has the following composition (mean of five analyses):

| SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | CaO. | MgO. | K ₂ O + Na ₂ O. | H ₂ O. | Total. | Sp. gr. |
|--------------------|----------------------------------|----------------------------------|------|------|------|---------------------------------------|-------------------|--------|---------|
| 49.73 | 29.67 | 4.03 | 0.67 | 0.27 | 0.60 | 9.31 | 5.35 | 99.63 | 2.813 |

L. J. S.

Sodalite from Kishengarh, India. ERNEST W. VREDENBURG (*Records Geol. Survey, India*, 1904, 31, 43—44).—Masses of sodalite, up to a foot across, occur in veins of elæolite-pegmatite in the neighbourhood of Kishengarh, in Rajputana. It is of a bright blue colour, or colourless and transparent. When kept in the dark for a few

weeks, the colourless variety assumes a pink colour, which rapidly disappears again on exposure to light. Analysis of the blue sodalite gave :

| SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | CaO. | Na ₂ O. | SO ₃ . | Cl. | Loss on ignition. | Total, less O for Cl. | Sp. gr. |
|--------------------|----------------------------------|----------------------------------|-------|--------------------|-------------------|------|-------------------|-----------------------|---------|
| 38.055 | 31.30 | trace | 0.001 | 24.77 | trace | 7.18 | 0.82 | 100.508 | 2.27 |

L. J. S.

A Mineral allied to Montmorillonite from New South Wales. CHARLES ANDERSON (*Records Australian Museum*, 1903, 5, 67—68).—The mineral is amorphous, clay-like, and white with a tinge of pink ; when first found, it was gelatinous. Over sulphuric acid, there is a loss of 10.74 per cent. of water, and at 100° a further loss of 1.16 per cent., which is reabsorbed when the mineral is exposed to moist air. Including this amount of water in the following analysis, the formula is $\text{Al}_2\text{O}_3, 4\text{SiO}_2, 6\text{H}_2\text{O}$.

| SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | MgO. | CaO. | Alkalis. | H ₂ O at 100°. | H ₂ O > 100°. | Total. |
|--------------------|----------------------------------|----------------------------------|-------|------|----------|---------------------------|--------------------------|--------|
| 52.72 | 21.28 | 0.87 | trace | 1.44 | traces | 11.90 | 12.54 | 100.75 |

L. J. S.

Sapphirine-bearing Rock from India. C. S. MIDDLEMISS (*Records Geol. Survey, India*, 1904, 31, 38—42).—A medium-grained rock, composed of hypersthene, sapphirine, biotite, and hercynite, occurs as a thin band associated with pyroxene-granulite and norite in the schists of the Vizagapatam district. The dark bluish-grey sapphirine has the same characters as the Greenland mineral ; there is, however, a good cleavage in one direction. Sp. gr. 3.539. Analysis by T. R. Blyth gave (after deducting about 10 per cent. of hercynite) the following results, agreeing with the formula $\text{MgO}, 2\text{FeO}, 6\text{Al}_2\text{O}_3, 2\text{SiO}_2$:

| SiO ₂ . | Al ₂ O ₃ . | FeO. | MgO. | CaO. | H ₂ O at 100°. | Loss on ignition. | Total. |
|--------------------|----------------------------------|-------|------|------|---------------------------|-------------------|--------|
| 12.55 | 67.06 | 16.21 | 3.97 | 0.17 | 0.25 | 0.54 | 100.75 |

L. J. S.

Connection between the Optical Characters and the Chemical Composition of Vesuvianite. CARL KLEIN (*Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 653—658).—Between the optically positive and negative varieties of vesuvianite there is a series in which there are abnormal arrangements in the coloured rings of the optic figures ; and, as with apophyllite, the optically positive and abnormal varieties pass into the optically negative when the crystals are strongly heated. In apophyllite, this change is due to loss of water and fluorine ; this is also probably the case with vesuvianite, in which the different optical varieties appear to have no connection with the presence of boron or the relative amounts of ferric and ferrous oxides. The mean of 83 analyses of vesuvianite is given below. The optically negative variety contains about 2.6 per cent. of water and fluorine, and this

increases in amount, through the abnormal varieties, to about 3 per cent. in the optically positive.

| SiO ₂ . | Al ₂ O ₃ + Fe ₂ O ₃ . | CaO. | MgO + FeO. | Alkalis. | H ₂ O + F. | Total. |
|--------------------|---|------|------------|----------|-----------------------|--------|
| 37.75 | 20.0 | 35.5 | 3.0 | 1.0 | 2.75 | 100.0 |

L. J. S.

Chemical Nature of Cimolite. W. SMIRNOFF (*Zeit. Kryst. Min.*, 1904, 39, 625—626; from *Trav. Soc. Imp. Natur. St. Pétersbourg*, 1902, 33, 214—223, 226—227).—The following analysis of cimolite, from Argentiera, Grecian Archipelago, agrees with the formula (Ca,Mg)SiO₃.7Al₂Si₃O₉.11H₂O. Analyses are also given of the portions soluble in hydrochloric acid and in sodium hydroxide solution. It is concluded that cimolite is not a definite chemical compound, but a kaolin-like product of weathering.

| SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | CaO. | MgO. | H ₂ O. | Total. |
|--------------------|----------------------------------|----------------------------------|------|------|-------------------|--------|
| 56.27 | 28.36 | 1.74 | 2.63 | 1.87 | 8.32 | 99.19 |

L. J. S.

A Bole-like Mineral from the Southern Urals. N. SURGUNOFF (*Zeit. Kryst. Min.*, 1904, 39, 623; from *Bull. Soc. Imp. Natur. Moscou*, 1902, 16, 511—513).—In cavities of the brown iron ore of the Verchne-Bulansk mine there is frequently found a reddish-brown, clayey substance in compact masses with a waxy fracture. The following analysis shows that the mineral in question is allied to bole or chloropal.

| SiO ₂ . | Fe ₂ O ₃ . | Al ₂ O ₃ . | CaO. | MgO. | Na ₂ O. | H ₂ O. | Total. |
|--------------------|----------------------------------|----------------------------------|------|------|--------------------|-------------------|--------|
| 39.74 | 25.06 | 14.12 | 0.95 | 0.58 | 2.88 | 16.87 | 100.20 |

L. J. S.

Monazite from New South Wales. CHARLES ANDERSON (*Records Australian Museum*, 1904, 5, 258—262).—Monazite has been previously recorded from two localities in New South Wales, but it has not hitherto been found *in situ*. The occurrence now described is of small crystals and grains of monazite embedded in the quartz and decomposed felspar of a pegmatite-vein in granite, at Blatherarm Creek, near Deepwater. Analysis gave:

| P ₂ O ₅ . | Ce ₂ O ₃ . | (La,Di) ₂ O ₃ . | (Y,Er) ₂ O ₃ . | ThO ₂ . | SiO ₂ . | (Al,Fe) ₂ O ₃ . | H ₂ O. | Total. | Sp. gr. |
|---------------------------------|----------------------------------|---------------------------------------|--------------------------------------|--------------------|--------------------|---------------------------------------|-------------------|--------|---------|
| 28.20 | 35.70 | 30.73 | trace | 1.63 | 0.49 | 2.23 | 0.34 | 99.32 | 5.119 |

L. J. S.

Analyses of Rocks. FRANK W. CLARKE (*Bull. U.S. Geol. Survey*, 1904, 228, 1—375).—This is a new edition of Bulletin No. 168 (1900) (Abstr., 1901, ii, 66), and gives a collection of 1672 analyses of crystalline and sedimentary rocks (including meteorites, clays, soils, &c.) made in the laboratory of the United States Geological Survey

during the years 1880—1903. The means of all the determinations made in these analyses are :

| SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | MgO. | CaO. | Na ₂ O. | K ₂ O. | H ₂ O at 100°. | H ₂ O > 100°. |
|--------------------|----------------------------------|----------------------------------|---------------------------------|--------------------|--------|--------------------|-------------------|------------------------------|--------------------------|
| 60.91 | 15.28 | 2.63 | 3.46 | 4.13 | 4.88 | 3.45 | 2.98 | 0.41 | 1.49 |
| TiO ₂ . | ZrO ₂ . | CO ₂ . | P ₂ O ₅ . | S. | Cl. | F. | BaO. | SiO. | |
| 0.73 | 0.03 | 0.53 | 0.26 | 0.11 | 0.07 | 0.02 | 0.11 | 0.04 | |
| MnO. | NiO. | Cr ₂ O ₃ . | V ₂ O ₃ . | Li ₂ O. | Total. | | | | |
| 0.10 | 0.03 | 0.05 | 0.03 | 0.01 | 101.74 | | | | |

L. J. S.

Weathering of the Ore-bearing Rock of Mount Magnitnaia. JÓZEF MOROZEWICZ (*Zeit. Kryst. Min.*, 1904, 39, 612—613; from *Verh. russ. min. Ges.*, 1903, 40, 62—69. Compare this vol., ii, 51).—The rock examined is an augite-diorite. When fresh (anal. II), it consists of plagioclase, yellowish-green augite, magnetite, a little orthoclase, &c. The augite constitutes 34 per cent. of the rock, and has the composition given under I, corresponding with the formula $3\text{CaMgSi}_2\text{O}_6, \frac{1}{2}\text{CaFe}''\text{Si}_2\text{O}_6, \frac{5}{9}\text{MgAl}_2\text{SiO}_6, \frac{5}{9}\text{Na}_2\text{Fe}_2''' \text{SiO}_6$. Analyses III and IV are of the rock in different stages of weathering; III is of a compact, ashen-grey mass, and IV of a cavernous, yellowish-grey, kaolin-like mass. Microscopical and chemical study shows that the following is the order of the weathering processes: (1) bleaching of the rock, the iron oxides being dissolved out and in part redeposited in the crevices of the rock; (2) the chloritisation of the augite and the formation of garnet microlites; (3) the kaolinisation of the feldspar.

| | SiO ₂ . | TiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | Mn ₂ O ₃ . | CaO. | MgO. | K ₂ O. | Na ₂ O. | H ₂ O. | Total. | Sp. gr. |
|------------|--------------------|--------------------|----------------------------------|----------------------------------|------|----------------------------------|-------|------|-------------------|--------------------|-------------------|--------|---------|
| I. 47.14 | 0.06 | 5.24 | 7.26 | 6.30 | 0.80 | 16.01 | 13.20 | 0.55 | 2.67 | 0.95 | 100.18 | 3.200 | |
| II. 46.97 | 0.14 | 16.16 | 10.66 | 4.38 | 0.75 | 9.02 | 4.56 | 1.26 | 4.47 | 1.74 | 100.40 | 2.988 | |
| III. 50.42 | 0.07 | 16.72 | 4.32 | 2.70 | 0.68 | 13.36 | 3.77 | 1.52 | 4.24 | 2.24 | 100.04 | 2.918 | |
| IV. 47.22 | trace | 20.09 | 5.51 | 2.02 | 0.66 | 6.93 | 4.39 | 1.52 | 2.56 | 8.78 | 99.78 | 2.604 | |

L. J. S.

Dioritic Rock from Lower Austria. JÓZEF MOROZEWICZ (*Zeit. Kryst. Min.*, 1904, 39, 610; from *Verh. russ. min. Ges.*, 1903, 40, 113—128).—A peculiar rock from the Kremsthal, in Waldviertel, was described by F. Becke in 1882 as an anorthite-diorite-schist. It consists of white bytownite (59½ per cent.; analyses I and II); pale green hornblende (32 per cent.; anal. III); a pyroxene (?) (7 per cent.; anal. IV) of very remarkable composition; limonite (½ per cent.), &c. The bulk analysis of the rock is given under V.

| | SiO ₂ . | TiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | MnO. | CaO. | MgO. | K ₂ O. | Na ₂ O. | H ₂ O. | S. | Total. | Sp. gr. |
|------------|--------------------|--------------------|----------------------------------|----------------------------------|-------|-------|-------|------|-------------------|--------------------|-------------------|----|--------|---------|
| I. 49.55 | — | 32.36 | 0.13 | — | — | 15.33 | — | — | 3.25 | 0.25 | — | — | 100.88 | 2.722 |
| II. 49.32 | — | 32.47 | 0.13 | — | — | 15.20 | — | 0.16 | 2.93 | 0.25 | — | — | 100.46 | 2.728 |
| III. 43.71 | 0.31 | 14.98 | 2.30 | 10.72 | 0.30 | 11.46 | 11.70 | 0.65 | 2.13 | 1.48 | — | — | 99.74 | 3.171 |
| IV. 47.72 | trace | 28.27 | — | 0.72 | — | 16.88 | 0.50 | — | 2.10 | 3.78 | — | — | 99.97 | — |
| V. 46.72 | trace | 26.33 | 1.34 | 3.52 | trace | 14.00 | 3.83 | 0.51 | 3.04 | 1.02 | 0.11 | — | 100.42 | 2.884 |

L. J. S.

The Persimmon Creek Meteorite. WIRT TASSIN (*Proc. U.S. National Museum*, 1904, 27, 955—959).—This meteorite, weighing 5·014 kilos., was found in 1893 on Persimmon Creek, Cherokee Co., North Carolina. It may be classed as a granular octahedrite containing numerous troilite and some silicate areas. On treating with dilute hydrochloric acid ($1\text{HCl} : 25\text{H}_2\text{O}$), the hydrogen sulphide evolved corresponded with 22·5 per cent. of sulphur; analysis of the soluble portion gave I. The insoluble residue included schreibersite (anal. II; sp. gr. 7·17), tænite (III; formula, Fe_8Ni), olivine (IV; sp. gr. 3·39), and carbon.

| | Fe. | Ni. | Co. | Cu. | Mn. | P. | SiO_2 . | MgO. | FeO. | Al_2O_3 . | Pt. | Total. |
|------|-------|-------|------|------|------|-------|------------------|-------|-------|---------------------------|-------|--------|
| I. | 94·36 | 3·72 | 0·25 | 0·29 | 0·01 | 0·27 | 0·81 | trace | — | trace | trace | 99·71 |
| II. | 69·33 | 17·26 | — | — | — | 12·50 | — | — | — | — | — | 99·09 |
| III. | 85·00 | 14·50 | — | — | — | 1·60 | — | — | — | — | — | 100·50 |
| IV. | — | — | — | — | — | — | 39·10 | 48·20 | 12·30 | — | — | 99·60 |

L. J. S.

Meteorite of Bjurböle. WILHELM RAMSAY and LEON H. BORGSTRÖM (*Bull. Comm. Géol. Finlande*, 1902, No. 12, 1—28).—This meteorite fell on March 12, 1899, breaking through the ice on the Finnish coast at Bjurböle, near Borgå. Several fragments were collected, the largest weighing 80·2 kilos.; the total weight was estimated at 400 kilos. It is a chondritic stone, containing nickel-iron (7·14 per cent.), troilite, schreibersite, chromite, enstatite (and bronzite), anorthite, olivine, maskelynite (?), and glass. A detailed description is given of the microscopical structure of the chondrules. The following is the composition of the stone :

| Fe. | Ni. | Co. | P. | FeS. | SiO_2 . | Al_2O_3 . | Cr_2O_3 . | FeO. | NiO. |
|------|------|------|------|-------|-------------------|---------------------------|---------------------------|-------|------|
| 6·38 | 0·72 | 0·04 | 0·14 | 5·44 | 41·06 | 2·55 | 0·59 | 13·80 | 0·07 |
| | | MnO. | CaO. | MgO. | K ₂ O. | Na ₂ O. | Total. | | |
| | | 0·12 | 1·82 | 25·75 | 0·32 | 1·24 | 100·04 | | |

L. J. S.

The Narraburra Meteorite. ARCHIBALD LIVERSIDGE (*J. and Proc. Roy. Soc. New South Wales*, 1904, 37, 234—242, with 12 plates).—This iron, found in 1885 on Narraburra Creek, Temora, New South Wales, weighed 70 lb. 14 oz., and had sp. gr. 7·57. Widmanstätten figures are prominently developed, and eight parallel sections were cut to show the structure of the mass in different parts. Analysis gave :

| Fe. | Ni. | Co. | Cu. | P. | S. | C. | Resinous Insol. | Pt. | Au. | Total. |
|--------|-------|-------|-------|-------|-------|----------|-----------------|-------|-------|----------------|
| 88·605 | 9·741 | 0·474 | 0·009 | 0·429 | trace | not det. | matter. in HCl. | 0·008 | 0·720 | traces? 99·986 |

L. J. S.

Chemical and Geological Studies of Different Springs in the North of Madagascar. GEORGES LEMOINE and PAUL LEMOINE (*Compt. rend.*, 1904, 139, 248—254).—The paper contains descriptions and analyses of eight thermal mineral waters collected in two different regions in the North of Madagascar, and also of three samples of

normal water from the same districts ; the mineral waters are characterised by the large proportion of sodium hydrogen carbonate they contain, varying from 0·12 to 1·58 grams per litre, and due to the amount of sodium salts in the volcanic rocks of the district (compare Lacroix, *Compt. rend.*, 1901, 132, 439).

M. A. W.

Physiological Chemistry.

Heteromorphism of Horse's Hæmoglobin. M. UHLIK (*Pflüger's Archiv*, 1904, 104, 64—88).—In addition to the ordinary rhombic crystals, true hexagons are also obtainable of horse's hæmoglobin. The methods by which this can be accomplished are described fully, and the crystals figured. Viscosity of the blood and a low temperature appear to be the principal factors operating in the production of hexagons. The meaning of such heteromorphism is discussed, but not settled.

W. D. H.

Effect of Intravenous Injection of Formaldehyde and Calcium Chloride on the Hæmolytic Power of Serum. C. C. GUTHRIE (*Amer. J. Physiol.*, 1904, 12, 139—148).—The intravenous injection of formaldehyde and of calcium chloride attenuates the hæmolytic action of serum, although not so markedly as in experiments *in vitro*.

W. D. H.

The Gastric Juice of New-born Dogs. W. GMELIN (*Pflüger's Archiv*, 1904, 103, 618—626).—Cohnheim and Soetbeer (*Zeit. physiol. Chem.*, 37, 467) state that new-born dogs secrete what Pawloff calls "psychical" gastric juice. In the present research, Pawloff's operation was found to be too complex for such small animals, and a simpler one was used. The juice does not contain hydrochloric acid until about the 21st day of life, although lactic acid was occasionally noted. Reflex secretion does not occur before the 18th day. After that date, flesh diet stimulates the secretion of more acid than milk does. During the first few days of life, milk is mainly digested in the intestine, where also Weinland's antiferments were found.

W. D. H.

The Chemical Combination and Action of Absorbed Phosphorus in the Body. VÁCLAV PLAVEC (*Pflüger's Archiv*, 1904, 104, 1—63).—Absorbed phosphorus does not act in the free form, for the breathing of compressed oxygen or of ozone has no influence on the course of the poisoning. After absorption, phosphorus, given in the free state, is combined as an oxide or as a compound in the protoplasm. In the blood, the higher the body temperature and the more oxyhæmoglobin it contains, the greater and more rapid is the union of phosphorus.

W. D. H.

Can the Small Intestine absorb Calcium Stearate? E. A. KNAUER (*Pflüger's Archiv*, 1904, 104, 89—108).—The experiments recorded on dogs and rabbits yield no confirmation of the statement that the small intestine can absorb calcium soaps. W. D. H.

The Action of Certain Antiseptics on Pepsin. JUL. A. GROBER (*Pflüger's Archiv*, 1904, 104, 109—118).—Toluene and chloroform have a harmful influence on enzymes, of which pepsin was particularly investigated. W. D. H.

Effect of Inanition on the Brain of the Rat. SHINKISHI HATAI (*Amer. J. Physiol.*, 1904, 12, 116—127).—Partial starvation in the white rat stops the growth of the brain, and causes in full-grown animals an appreciable loss of brain substance. The percentage of water and of ether-alcohol extracts is affected to a very slight degree. W. D. H.

Reducing Action of the Animal Organism under the Influence of Cold. CHRISTIAN A. HERTER (*Amer. J. Physiol.*, 1904, 12, 128—138).—A considerable fall in body temperature is attended by a diminished reduction of methylene-blue to leuco-methylene-blue, and this result is specially striking in the case of the muscles, including the heart and diaphragm and the grey matter of the central nervous system. Experiments on the effect of febrile temperatures are in contemplation. W. D. H.

Structural Changes of Ova in Anisotonic Solutions and Saponin. TORALD SOLLMANN (*Amer. J. Physiol.*, 1904, 12, 99—115).—Anisotonic solutions cause decomposition and solution of the cytoplasm of ova, raising the osmotic pressure to such a degree that the cell may swell in hypertonic solutions. The behaviour of the erythrocytes of annelids towards laking agents closely resembles that of vertebrate corpuscles. W. D. H.

Elimination of Endogenous Uric Acid. ELBERT W. ROCKWOOD (*Amer. J. Physiol.*, 1904, 12, 38—54).—Burian, Schur, Walker Hall, and others maintain that the endogenous purine output is variable for different individuals, but constant in quantity for the same person. This contention is supported by the present experiments. The individual constancy is striking when various diets are given in the same person, and when the same diet is given to different persons. W. D. H.

Effect of Alcohol on the Excretion of Uric Acid in Man. S. P. BEEBE (*Amer. J. Physiol.*, 1904, 12, 13—37).—The experiments were conducted on men unaccustomed to the use of alcohol in any form. Moderate doses of various alcoholic liquids (ale, wine, &c.) were given. After some degree of immunity had been established, evidence of its proteid sparing effect was obtained; it may thus in a sense be regarded as a food. But this is counterbalanced by its harmful effect on the liver; the oxidation processes in this organ are

lessened, and an increase of uric acid excretion is the immediate result.

W. D. H.

Intermediary Purine Metabolism; the Production of Allantoin. LAFAYETTE B. MENDEL and BENJAMIN WHITE (*Amer. J. Physiol.*, 1904, 12, 85—94).—The intravenous injection of urates in cat and dog, like that of nucleic acid, causes an excretion of allantoin. This is most marked when the injection is made into the portal vein. Observations on rabbits gave negative results. The result in carnivora is interfered with by sulphonal. Allantoin is probably formed in the liver.

W. D. H.

Fate of Glycine in the Dog's System when injected Intravenously. SERGEI SALASKIN and KATHARINA KOWALEWSKY (*Zeit. physiol. Chem.*, 1904, 42, 410—414. Compare Stolte, *Hofmeister's Beitr.*, 5, 15; also Abstr., 1898, ii, 441).—A single injection of a considerable amount of glycine increases the amount of ammonia in the blood, the glycine is rapidly removed from the blood, a small amount is eliminated with the urine, and part is given up to the other tissues. Glycine is not found as such in the tissues, as it rapidly undergoes decomposition, yielding carbamide probably by the elimination of ammonium carbonate or carbamate.

J. J. S.

Behaviour of Aspartic Acid in the Animal Organism. ERNST SALKOWSKI (*Zeit. physiol. Chem.*, 1904, 42, 207—212).—It is shown that aspartic acid administered to dogs is eliminated in the urine as carbamide and not as uraminosuccinic acid. Possibly a small amount is eliminated undecomposed.

J. J. S.

Occurrence of Amino-acids in Urine, especially in Cases of Gout. ALEXANDER IGNATOWSKI (*Zeit. physiol. Chem.*, 1904, 42, 371—400).—Normal human urine contains only traces of amino-acids; even after subcutaneous injection of 6 grams of glycine, amino-acids cannot be detected in this liquid. Considerable amounts are sometimes found, however, (a) in cases of gout—in seven instances glycine was found and in three cases other amino-acids, probably leucine and aspartic acid; (b) in cases of pneumonia.

The method of detection was a modified form of that described by E. Fischer and Bergell (Abstr., 1903, i, 24. Compare Abderhalden and Bergell, *ibid.*, ii, 742). The urine is precipitated with lead acetate, the lead removed from the filtrate by means of hydrogen sulphide, the liquid evaporated at a temperature below 45° to half its bulk and then extracted for 3 hours with ether. The purified urine is then shaken for 9 hours with an ethereal solution of naphthalene- β -sulphonic chloride, care being taken to keep the solution faintly alkaline by means of potassium hydroxide. The addition of hydrochloric acid to the aqueous solution precipitates the naphthalene- β -sulphonyl derivatives of the amino-acids.

J. J. S.

The Combined Action of Proteolytic Enzymes. PHOEBUS A. LEVENE and L. B. STOOKEY (*Amer. J. Physiol.*, 1904, 12, 1—12).—When spleen and pancreas (mixed glands or extracts) act on egg

albumin or casein, the amount of digestion products is greater than the sum of the products when the two glands act separately. This is chiefly attributable to increase in the activity of the pancreatic enzyme, for if all the zymogen of the pancreas is converted into enzyme previously, the effect mentioned in the first paragraph is no longer noticeable. These experiments corroborate Schiff's view that the spleen facilitates the transformation of the pancreatic zymogen into the active enzyme. No similar action of the spleen on the liver was detected.

W. D. H.

Combustion of Carbohydrates. II. The Active Substance of the Pancreas. OTTO COHNHEIM (*Zeit. physiol. Chem.*, 1904, 42, 401—409. Compare Abstr., 1903, ii, 738).—To obtain the active principle of pancreas previously described, the following method is recommended. The pancreas is chopped up, thrown into boiling water, and evaporated to dryness. The residue is extracted several times with alcohol and the extracts evaporated to dryness. This residue is extracted with hot ether and the insoluble part dissolved in alcohol, filtered, evaporated, and again dissolved in alcohol. When required for use, the solution is evaporated and the residue dissolved in water, so that 10 c.c. of the solution = 1 gram pancreas. The substance closely resembles the product obtained by Magnus (this vol., ii, 628) from liver.

It is found that the addition of too large a quantity of the pancreas extract tends to retard the combustion of the sugar. The maximum results are obtained when 0.8 gram of pancreas is used with 75 grams of muscle.

Blood serum contains an acceptor similar to pancreas, and muscle from which the blood has not been entirely removed therefore acts in the same manner as muscle and pancreas extract, and the addition of much pancreas extract retards the combustion.

J. J. S.

The Influence of the Pancreas on the Composition of Proteid. PETER BERGELL and FERDINAND BLUMENTHAL (*Pflüger's Archiv*, 1904, 103, 627—631).—Fischer has shown that the pancreatic ferment easily hydrolyses peptides which contain tyrosine and leucine, but that it cannot destroy analogous compounds of alanine or glycine such as the dipeptide glycylglycine, $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$.

In a dog without a pancreas, the urine was free from proteid and peptone, but contained tyrosine in abundance: glycylglycine was injected subcutaneously in large quantities; no glycine appeared in the urine, and only traces of glycylglycine. In the normal animal, both are found; the pancreas being absent, the ability to decompose the dipeptide had disappeared. Feeding on tyrosine or substances containing it increases the amount in the urine; in healthy animals, this does not occur. The clinical importance of tyrosine in the urine in cases of pancreatic disease is noted.

W. D. H.

Composition of Gorgonian Corals. FRANK C. COOK (*Amer. J. Physiol.*, 1904, 12, 95—98).—Investigation of the iodine-containing organic material called gorgonin in several kinds of corals shows the

amount of sulphur to be less than 2 per cent., which is not so high as in Mediterranean species. Mercaptan was not obtained. Bromine was absent. The large amount of nitrogen and the failure to obtain carbohydrate groups show that gorgonin is not allied to chitin.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Velocity of Fermentation Reactions on the Addition of Chemically Indifferent Substances. HERMANN BRAEUNING (*Zeit. physiol. Chem.*, 1904, 42, 70—80).—It has been found that when part of the water in a process of fermentation is replaced by some chemically indifferent substance which is soluble in water, the velocity of the reaction is diminished. Among the examples given are addition of glycerol to invertase solution, to emulsin, zymase, pepsin, trypsin, or rennet, or even to yeast.

Carbamide has a retarding action on invertase and on yeast, whilst dextrose or lactose produces the same effect on trypsin. Examples are also quoted from other researches.

Two exceptions to the generalisation appear to exist. Weiss (*Zeit. physiol. Chem.*, 1902, 40, 488) states that the pancreatic fermentation of fibrin is not affected by dextrose, and Arnheim (*ibid.*, p. 238) that dextrose, milk sugar, or dextrin accelerates the autolysis of the liver ferment.

The addition of colloidal solutions of indifferent substances such as gum arabic has not always the same effect. J. J. S.

The Mechanism of Respiratory Combustion. Production of Citric Acid by Citromycetes. PIÉRRÉ MAZÉ and A. PERRIER (*Compt. rend.*, 1904, 139, 311—313).—The formation of citric acid in pure cultures of *Citromycetes* begins when the mould has nearly attained its maximum weight and the medium no longer contains nitrogen in a form capable of being assimilated; the young cells grow at the expense of the older ones, depriving them of their nitrogen and forming citric acid at the same time. *Citromycetes* can assimilate other ternary food-stuffs than sugar, for example mannitol, glycerol, alcohol, or the higher hydroxy-acids of the aliphatic series, citric acid being produced at the expense of these substances; moreover, the production of citric acid takes place equally well in cultures deprived of air; it is probable, therefore, that the formation of this acid is not due to the direct oxidation of sugar, but to the breaking down of the living substance itself. M. A. W.

Variations of Mineral Matters in Ripening Seeds. GUSTAVE ANDRÉ (*Compt. rend.*, 1904, 138, 1712—1714).—The amount of ash in lupin and haricot pods during the ripening period increases up to

a certain point and then diminishes. The decrease in the amount of ash is not proportional to the decrease in dry matter.

As regards the seeds, the amount of ash goes on increasing to the end. The percentage amount of ash, however, decreases during the ripening period.

The amounts of calcium and magnesium in the pods increase at the commencement of the ripening period and then diminish. The amount of potassium increases during the whole period, both in the pods and in the seeds. The phosphoric acid of the seeds increases up to the end, whilst in the case of the pods the accumulation which takes place in the first stages of ripening is followed by a loss. N. H. J. M.

Complete Extraction of Water and Gas from Seeds. PAUL BECQUEREL (*Compt. rend.*, 1904, 138, 1721—1723).—The results of experiments with peas indicated that the seed can be completely deprived of water and gas at a temperature of 50° by means of sulphuric acid or baryta in a vacuum.

The difficulty due to the tegument of the seed and to the albumen, which is often mucilaginous and becomes more and more impervious as desiccation proceeds, may be overcome by employing decorticated seeds or by cutting the tegument and albumen. N. H. J. M.

Mechanism of the Action of the Cytoplasm in Germinating Seeds. MAURICE NICLOUX (*Compt. rend.*, 1904, 139, 143—145. Compare this vol., ii, 508).—The acidity of germinating oleaginous seeds is due to two aliphatic acids derived from the fatty substance of the seed under the influence of the protoplasm, carbon dioxide, and water.

The same reaction may be produced with oils of various origin by means of mechanically-separated cytoplasm and water saturated with carbon dioxide. N. H. J. M.

Plant Acidity. EUGÈNE CHARABOT and ALEXANDRE HÉBERT (*Compt. rend.*, 1904, 138, 1714—1716).—The acidity due to volatile acids is always highest in the leaves. In shaded plants, however, the acidity is highest in the roots. The relations between the saturated volatile acids and the total volatile acids increases during the growth of leaves and stems and is greater in the stems than in the leaves.

The alkalinity of the ash is always greatest in the leaf. In absence of light, the amount of combined organic acids increases. Suppression of inflorescence reduces the amount of combined organic acids.

The whole of the results obtained accord with the view that organic acids are probably oxidation products of carbohydrates.

N. H. J. M.

Factors of Availability of Plant Food. GEORGE S. FRAPS (*Amer. Chem. J.*, 1904, 32, 1—13).—The amounts of available potassium and phosphoric acid in soil are somewhat increased by moisture. Calcium sulphate and carbonate diminish the amount of available potassium, and calcium carbonate reduces the amount of available phosphoric acid as well.

Starch and sawdust decrease the available phosphoric acid, but

increase the available potassium. In one case, the amount of available potassium was doubled. Stable manure has a similar effect on the potassium of the soil.

N. H. J. M.

Fly Agaric (*Amanita Muscaria*). WILHELM HEINISCH and JULIUS ZELLNER (*Monatsh.*, 1904, 25, 537—544).—This fungus was collected from Upper Styria and from the granite region of Southern Bohemia. The air-dried fungus is 14.9, and the ash 1.02—1.05 per cent. of the fresh material. The following is the composition of the ash; the numbers being percentages, the first for the ash of the Styrian and the second for that of the Bohemian fungus:—

| | I. | II. | | I. | II. |
|----------|-------|-------|----------------------------------|-------|-------|
| K | 44.00 | 41.10 | PO ₄ | 23.13 | 20.77 |
| Na | 0.24 | 0.58 | SO ₄ | 3.08 | 2.46 |
| Mg | 1.37 | 1.25 | Cl | 6.88 | 6.41 |
| Ca | 0.53 | 0.21 | SiO ₃ (soluble)..... | 0.88 | 7.38 |
| Al | 2.46 | 1.26 | SiO ₂ (insoluble) ... | 5.87 | 8.33 |
| Fe | 0.12 | 0.06 | CO ₃ O, loss..... | 11.44 | 10.19 |

(With traces of Mn in each.)

On extracting the air-dried substance with light petroleum (b. p. 40—70°), and distilling off the solvent finally at 130° in an atmosphere of carbon dioxide, an oil is obtained, which, at the ordinary temperature, deposits a crystalline substance melting at 42—44° and solidifying completely at 8—9°. It has a sp. gr. 0.9166 at 15°, n_D , 1.460—1.470 at 20°, hydrolysis number 227, acid number 177, iodine number 82, Hehner's number 97.93, Reichert-Meissl's number 4.4. The insoluble fatty acid melts at 10°. The oil contains 7.42 per cent. of lecithin, and also ergosterin (Tanret, *Abstr.*, 1889, 407), glycerol, choline, butyric, palmitic (the only solid acid present), and oleic acids, the last of these acids constituting 90 per cent. of the total fat.

G. Y.

Analytical Chemistry.

Use of Hydrazine Sulphate in Gasometric Analysis. J. DE GIRARD and A. DE SAPORTA (*Bull. Soc. chim.*, 1904, [iii], 31, 905—907. Compare Purgotti, Abstr., 1897, ii, 349).—The authors find that when solutions of copper and hydrazine sulphates are mixed, a crystalline precipitate of the double sulphate, $\text{CuSO}_4 \cdot \text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$, is formed, which is not decomposed on addition of sodium chloride, as Purgotti supposed (*loc. cit.*), but is attacked by sodium hydroxide, forming cuprous oxide and liberating nitrogen. Measurement of the nitrogen liberated permits of the estimation of copper, every 2 grams of copper sulphate furnishing about 50 c.c. of the gas. This method may be applied in-

directly to the estimation of reducing sugars by dissolving the cuprous oxide formed, when these sugars are boiled with excess of Pasteur's solution, in a mixture of nitric and sulphuric acids and estimating with hydrazine sulphate the amount of copper sulphate produced. The liberation of nitrogen in the cold by the interaction of solutions of hydrazine sulphate and sodium nitrite may similarly be employed for the estimation of the latter salt. T. A. H.

Employment of Persulphate for Quantitative Separations. MAX DITTRICH and C. HASSEL (*Zeit. anal. Chem.*, 1904, 43, 382—387. Compare Abstr., 1902, ii, 693; 1903, ii, 243, 254).—The authors ascribe the failure of v. Knorre to effect the complete separation of manganese from other metals by ammonium persulphate (this vol., ii, 213) to the very large quantities of material employed, and the impossibility of washing completely such large precipitates. They have repeated their experiments, and, working with about 0.1 gram of Mn_2O_4 to which 0.5 gram of a salt of zinc, cadmium, copper, nickel, calcium, or magnesium was added, have obtained results for the manganese which differed by only a few tenths of a milligram from the quantity taken, and where they examined the manganese precipitate for the other metal (for example, copper and cadmium) not a trace could be detected. Even when employing quantities as large as those taken by v. Knorre, they were able by a second precipitation to obtain a complete separation in the case of copper.

M. J. S.

Estimation of Nitric Acid with Ferrous Sulphate. G. BAILHACHE (*Bull. Soc. chim.*, 1904, [iii], 31, 843—846. Compare Debourdeaux, this vol., ii, 147).—The apparatus consists of a 250 c.c. flask closed by an india-rubber bung carrying a stoppered dropping funnel and a small serpentine condenser, to the upper extremity of which is joined a small U-tube of narrow bore ending in a bulb containing a little mercury.

The standard solution contains 110 grams of ferrous sulphate and 75 c.c. of sulphuric acid per litre. With 50 c.c. of this, previously placed in the flask, 30 c.c. of strong sulphuric acid are mixed; 20 c.c. of a saturated solution of sodium hydrogen carbonate are then added slowly through the dropping funnel, the liquid being meanwhile heated to the boiling point. To the hot liquid, 10 c.c. of the nitrate solution (about 5 per cent.) are added through the dropping funnel; the stopper is then closed and the heating continued until no more gas is evolved. The last traces of the nitrate solution are washed through the dropping funnel with a saturated solution of sodium hydrogen carbonate and the unchanged ferrous sulphate is estimated in the usual way with potassium permanganate or dichromate. T. A. H.

Method for the Determination of Chloric Acid. WALTER S. HENDRIXSON (*Amer. Chem. J.*, 1904, 32, 242—246).—Metallic iron readily reduces free chloric acid, even in very dilute solutions. On adding an excess of sulphuric acid and then iron to a solution of chloric acid or a chlorate, reduction proceeds at the ordinary tempera

ture. Ferric sulphate is at first formed, and the end of the reaction is indicated by the disappearance of the yellow colour. The solution is titrated with silver nitrate. The method is also applicable to bromates, but perchlorates are not attacked.

C. H. D.

Estimation of Phosphates in Natural Waters. AZARIAH T. LINCOLN and PERRY BARKER (*J. Amer. Chem. Soc.*, 1904, 26, 975—980).—The authors have rendered Schreiner's method for estimating minute quantities of phosphates (*J. Amer. Chem. Soc.*, 1901, 23, 96; 1902, 24, 735) applicable to waters which contain a larger proportion of silica than phosphoric acid, by adding a small known excess of a standard solution of a phosphate. The procedure then becomes exactly the same as described by Schreiner.

W. A. D.

Estimation of Phosphorus or Arsenic in Organic Compounds. C. MONTHULÉ (*Ann. Chim. anal.*, 1904, 9, 308—309).—A solution is prepared by dissolving magnesium oxide in nitric acid of sp. gr. 1.38, so that 100 c.c. of liquid will contain 10 grams of magnesia. The substance to be tested, if solid, is immersed in the reagent contained in a porcelain dish, and the mass is evaporated to dryness gradually and finally subjected to a red heat. If the carbon does not burn off readily, a second treatment with nitric acid is necessary.

The residue is now dissolved in dilute hydrochloric acid, and the phosphorus or arsenic is then precipitated as magnesium ammonium phosphate or arsenate by adding ammonia.

L. DE K.

Detection of Arsenic in Normal Animal Tissues by means of the Biological Method. M. SEGALE (*Zeit. physiol. Chem.*, 1904, 42, 175—180. Compare Gautier, *Abstr.*, 1900, ii, 670; Hödlmoser, 1901, ii, 673; Cerny, 1902, ii, 274).—Arsenic can readily be detected in practically all animal tissues by the aid of Gosio's method with *Penicillium brevicaulis* (*Abstr.*, 1897, ii, 381; 1901, ii, 182, 193), provided that the tissue is first subjected to autolysis in the presence of a few drops of chloroform for 20—60 days at 37°. The only tissues which give negative results are horn, hair, feathers, &c., which do not undergo autolysis under the conditions mentioned.

Tellurium gives a very similar result; the odour is, however, somewhat different and the reaction not nearly so delicate as with arsenic. Selenium gives quite a different odour.

J. J. S.

Titration of Ammonium Salts. FERDINAND JEAN (*Ann. Chim. anal.*, 1904, 19, 257).—Ten grams of the sample are put into a 500 c.c. flask, dissolved in 250 c.c. of water, and mixed with about 200 c.c. of a solution of pure sodium hydroxide (38 grams per litre). The whole is then diluted to 500 c.c. and allowed to settle.

Twenty-five c.c. are pipetted off and titrated with $N/2$ oxalic acid, using lacmoid as indicator. Another 25 c.c. are diluted with 30 c.c. of water and boiled in a conical flask for half an hour, 20 c.c. of water are added, and the remaining alkali is again titrated. The difference in the titrations represents the volatile alkali or the ammonia.

L. DE K.

Estimation of Calcium. OSWALD BRUCK (*Zeit. angew. Chem.*, 1904, 17, 953).—A criticism of Kettler's method (this vol., ii, 517) Conversion into calcium sulphate, besides not being novel, is less simple than the time-honoured method of treating the ignited calcium oxalate with ammonium carbonate and weighing as carbonate.

L. DE K.

Rapid Method for the Estimation of Lime in a Cement. BERNARD ENRIGHT (*J. Amer. Chem. Soc.*, 1904, 26, 1003—1006).—0.5 gram of the finely powdered cement, suspended in 100 c.c. of hot water in an evaporating dish, is dissolved by adding 30 c.c. of hydrochloric acid (1:1); after adding a few drops of bromine water, the solution is boiled until only a few flakes of silica remain, dilute ammonia is added, the solution again boiled for 1 minute, and filtered. The precipitate is washed back into the dish, 10 c.c. of hydrochloric acid are added, the solution diluted to 100 c.c., and again precipitated with ammonia; the precipitate contains all the ferric oxide and alumina and the greater part of the silica. The two filtrates are mixed, slightly acidified with hydrochloric acid, and precipitated hot with ammonium oxalate; the solution is boiled and hot dilute ammonia added, with constant stirring, until an excess equivalent to about 5 c.c. of concentrated ammonia is present. After boiling for 5 minutes, precipitation will be complete after another 15 minutes. The precipitate is then transferred to a conical flask, dissolved in hot dilute sulphuric acid, and the solution titrated with a potassium permanganate solution which has previously been standardised by means of a standard cement.

W. A. D.

Analysis of Portland Cement. BERTRAM BLOUNT (*J. Amer. Chem. Soc.*, 1904, 26, 995—1003).—The "insoluble residue" is best determined by dissolving the cement in hydrochloric acid, evaporating the solution to dryness, redissolving the residue in hydrochloric acid, filtering, washing, extracting the precipitated silica with aqueous sodium carbonate, and collecting the final insoluble residue. A comparison is made of the results of this method with those obtained by Hillebrand's process. The latter gives an insoluble residue which is a cementitious material rather than a true insoluble residue.

It is also shown that a double evaporation in estimating the silica of a cement is unnecessary; that the silica obtained in a cement analysis contains neither ferric oxide nor alumina, and that, under these conditions, the amount of silica carried down in the precipitation of these oxides by ammonia is extremely small.

W. A. D.

Colorimetric Estimation of Magnesium. OSWALD SCHREINER and W. S. FERRIS (*J. Amer. Chem. Soc.*, 1904, 26, 961—967).—In this method, which gives good results in the estimation of minute quantities, the magnesium is precipitated by means of potassium hydrogen phosphate after adding a few drops of ammonium oxalate to prevent the co-precipitation of calcium salts present; the precipitate, after being thoroughly washed, is dissolved in nitric acid, and, ammonium molybdate having been added, the solution is compared colorimetrically with magnesium solutions of known concentration.

In order to obtain successful results, the details given by the author have to be followed closely.

W. A. D.

Detection of Cadmium in Silver Ornaments. LOUIS L'HÔTE (*Ann. Chim. anal.*, 1904, 9, 241—242).—Cadmium is frequently substituted to some extent for copper in silver alloys. This may be readily detected by heating the metal in a cupel or in a combustion tube after addition of some lead, or simply by heating the metal over a Bunsen flame and condensing the fumes on the bottom of a tube filled with water.

The brown sublimate so obtained is then tested for cadmium by the usual reagents.

L. DE K.

Use of Complex Salts in Electrolytic Analysis: Separation of Copper from Arsenic and Antimony, Nickel from Zinc, and Zinc from Iron. AUGUSTE HOLLARD and L. BERTIAUX (*Bull. Soc. chim.*, 1904, [iii], 31, 900—904).—The deposition of small quantities of arsenic with the copper in the electrolytic estimation of this metal is avoided if the operation be conducted in nitric acid solution to which a small quantity of ferric sulphate has been added, since, under these conditions, the arsenic is maintained in the state of arsenic acid throughout the experiment. Antimony may be eliminated similarly by the addition of lead sulphate to the mixture, the lead peroxide formed on the anode serving to retain this impurity (Hollard, Abstr., 1903, ii, 294).

In addition to the methods already described for the electrolytic separation of zinc and nickel (Abstr., 1903, ii, 335, and this vol., ii, 92), the deposition of the former metal may be prevented by converting it into a zinc-ammonium nitrite, provisionally represented by the formula $\text{Am}_2[\text{Zn}(\text{NO}_2)_2]_2$. To the solution of the sulphates of the two metals, magnesium sulphate (5 grams) and ammonia solution, 22° B. (20 c.c.), are added. The liquid is then made slightly acid with sulphuric acid, and ammonium nitrate (12.5 grams) added, followed by a saturated solution of sulphur dioxide (25 c.c.). The excess of sulphur dioxide is removed by ebullition, the liquid is then somewhat diluted and solution of ammonia, 22° B. (25 c.c.), added, and the whole made up to 300 c.c. A current of 1 ampere is used at 85°; the deposit of nickel is complete in a few hours.

Zinc may be separated from iron by converting the latter into potassium ferrocyanide, as already described (Abstr., 1903, ii, 513). The electrolysis is carried out in the cold with a current of 0.4 ampere. The zinc deposited may contain from 0.039 to 0.103 per cent. of iron.

It is pointed out that the method of separating and estimating antimony described by A. Fischer (Abstr., 1903, ii, 616) had already been published by one of the authors (Hollard, Abstr., 1900, ii, 442, and 1903, ii, 455).

In the cases described above, the metals present in the complex ions are not deposited on the cathode, but with the double cyanides of gold, silver, cadmium, and mercury with potassium the heavy metals are deposited, probably because in these cases the complex ions are themselves further dissociated.

T. A. H.

Bismuth Method for the Estimation of Manganese. ANDREW A. BLAIR (*J. Amer. Chem. Soc.*, 1904, 26, 793—801).—The bismuth method for the estimation of manganese, originally proposed by Schneider, is based on the fact that a manganous salt in the presence of an excess of nitric acid is oxidised to permanganic acid by bismuth tetroxide. The permanganic acid formed is very stable in nitric acid of sp. gr. 1.135 when the solution is cold. The excess of bismuth salt is filtered off and an excess of ferrous sulphate added to the filtrate, the amount necessary to deoxidise the permanganic acid being determined by titration with permanganate.

The author finds the method very accurate and rapid and gives details of the estimation of manganese in steel, pig iron, and iron and manganese ores. A. McK.

Estimation of Small Amounts of Ferric Iron by Acetylacetone. H. B. PULSIFER (*J. Amer. Chem. Soc.*, 1904, 26, 967—975).—Acetylacetone may be used in a colorimetric method for estimating traces of iron in nearly all those cases in which potassium thiocyanate has hitherto been employed. It has the advantage that the pink colour it produces with a ferric salt is remarkably permanent and nearly independent of temperature; moreover, very few inorganic salts which can exist in solution with ferric iron have any influence on the colour. The range over which acetylacetone can be used is greater than that of potassium thiocyanate; the smallest quantity of iron that can be detected is 0.000003 gram, and the largest with which the method can be used in a 50 c.c. tube is 0.0006 gram. Standard iron solutions are made by dissolving pure iron wire in a few c.c. of hydrochloric and nitric acids and suitably diluting; the final solution should not contain so much acid that, when placed in a Nessler cylinder, it appears pink by reflected light. The solutions which are compared with the standard solutions should have roughly the same acidity as these. To each 50 c.c. of the very dilute iron solution, 2 c.c. of a 0.5 per cent. solution of acetylacetone is added; this is sufficient, with the concentrations of iron given above, to produce the maximum coloration. W. A. D.

Electrolytic Separation of Nickel and Zinc. AUGUSTE HOLLARD and L. BERTIAUX (*Compt. rend.*, 1904, 138, 1605. Compare *Abstr.*, 1903, ii, 335; this vol., ii, 92).—In addition to the methods already described for the electrolytic separation of nickel and zinc, a third method consists in converting the zinc into a double nitrite of zinc and ammonium which does not yield zinc ions. The nickel and zinc, in the form of their sulphates, are treated successively with magnesium sulphate, ammonia, dilute sulphuric acid, ammonium nitrate, and sulphur dioxide, the excess of sulphur dioxide is boiled off, the liquid rendered alkaline with ammonia and diluted; electrolysis is effected with a current of 1 ampere at a temperature of 85° for several hours. M. A. W.

Action of Nitric and Acetic Acids on Alkali Chromates. AUGUSTE LEUBE (*Ann. Chim. anal.*, 1904, 9, 303—304).—In the assay of chrome iron ore, it is customary to treat with dilute nitric acid the

product of the disintegration with sodium carbonate in order to decompose the salts formed. The author has proved experimentally that under these conditions a very appreciable proportion of the chromic acid is reduced to a chromic salt and ultimately precipitated with the iron oxide on adding ammonia. Further experiments proved that this reduction also takes place to some extent in the cold.

Acetic acid behaves similarly to nitric acid.

L. DE K.

Volumetric Estimation of Vanadium and Chromium in the same Solution. EM. CAMPAGNE (*Bull. Soc. chim.*, 1904, [iii], 31, 962—965. Compare Abstr., 1903, ii, 761, and Nicolardot, this vol., ii, 369).—The chromium is converted into sulphate and the vanadium into divanadyl sulphate by the method already described (*loc. cit.*). The vanadium is then titrated with permanganate (*ibid.*), and, finally, excess of permanganate is added and the liquid boiled to convert the chromium sulphate into chromic acid. The excess of permanganate is eliminated by ebullition with portions of filter paper, and to the filtrate a known quantity of ferrous sulphate is added, and the portion unoxidised by the chromic acid is determined by titration with permanganate. In reality, the excess of ferrous salt reduces an equivalent portion of vanadic acid to divanadyl sulphate, and it is this which is titrated. The results are not affected by the presence of small quantities of ferric sulphate in the original liquid. If the quantity of chromium present is large compared with the vanadium, it is necessary to work with small quantities of the material, since the green colour of the chromium salt somewhat obscures the end reaction in the titration of the vanadium.

T. A. H.

Electrolytic Estimation of Bismuth. AUGUSTE HOLLARD and L. BERTIAUX (*Compt. rend.*, 1904, 139, 366—367).—To separate bismuth from copper, the bismuth is precipitated as phosphate by addition of phosphoric acid, and to facilitate the removal of any copper salt, the precipitated phosphate is washed with a solution containing ammonium hydrosulphide and potassium cyanide. The bismuth phosphate is then dissolved in dilute nitric acid, evaporated with sulphuric acid, the solution diluted, and electrolysed with a current of 0.1 ampere. Any small quantity of copper deposited with the bismuth is corrected for by a colorimetric determination.

To separate bismuth from lead, the authors precipitate the lead as sulphate, add alcohol, and electrolyse the solution directly without filtering. If the lead sulphate is filtered off, considerable quantities of bismuth are lost, and if alcohol is not added the appreciable solubility of the lead sulphate results in the deposition of lead along with the bismuth.

H. M. D.

Microchemical Detection of Gold by means of the Colloidal Coloration of Silk Fibres. JULIUS DONAU (*Monatsh.*, 1904, 25, 545—554. Compare Emich, Abstr., 1902, ii, 45, 351).—When a solution of gold chloride in hydrochloric acid is poured into a vessel which has been rinsed out with an aqueous solution of tannin, the solution gradually becomes purple and, on addition of sodium chloride, blue with precipitation of gold. With a greater amount of tannin,

the solution becomes green to blue. If the vessel has been rinsed with an aqueous solution of stannous chloride and pyrogallol, the purple colour appears on warming. When dipped into a dilute gold solution and heated in the benzene flame, a borax bead becomes ruby coloured; on longer heating, blue; and in presence of traces of gold, finally, colourless.

Silk and cotton fibres, treated either with tannin or with stannous chloride and pyrogallol, are used for the microchemical detection of gold. The silk fibres are coloured red with colloidal gold. The cotton wool shows a blue or dark coloration due to a suspension of gold particles. The most delicate reaction (detection of 0.000002 milligram of gold) is obtained with silk treated with stannous chloride and pyrogallol. These colours are destroyed by chlorine or bromine water, but not by acids or alkalis. The coloration of the silk fibre is prevented by the presence of free bases, concentrated mineral acids, arsenious or arsenic acids, silicates, free halogens, reducing agents, tartar emetic, or antimonates. Silver salts form, in the fibres, a yellow colour which disappears on adding nitric acid. G. Y.

Assay of Platinum, Gold and Silver Alloys. AUGUSTE HOLLARD and L. BERTIAUX (*Ann. Chim. anal.*, 1904, 9, 287—292).—A criticism of the method used by the French assayers which, although giving approximately the amount of gold and platinum, fails to indicate the true percentage of silver. The author states that the amount of gold actually found is generally 0.002 gram too low.

The silver may be accurately estimated as follows. A few decigrams of the alloy are dissolved in a mixture of 1 vol. of nitric and 5 vols. of hydrochloric acid and evaporated to a syrupy consistency. The residue is then freed from hydrochloric acid by evaporating twice with nitric acid. It is then dissolved in a few c.c. of water, mixed with two drops of hydrochloric and 2 c.c. of nitric acid, and, after boiling, diluted to 150 c.c. The silver chloride is then collected, dissolved in 30 c.c. of a 20 per cent. solution of potassium cyanide, and the metal is deposited electrolytically with the usual precautions. Its purity is ascertained by titration with thiocyanate as usual. L. DE K.

Use of Pumice to facilitate the Combustion of Organic Substances. MAURICE DUYK (*Ann. Chim. Anal.*, 1904, 9, 252—254).—The refractory substance (albumins, yeast, wool, &c.) is mixed with an equal weight of pumice (mesh 5) and then incinerated in a muffle or over a Bunsen flame. An ash free from carbon is thus obtained, which may be separated from the pumice by suitable solvents. L. DE K.

A Frequent Source of Error in the Analysis of Coal. JUST ALIX and ISIDORE BAY (*Compt. rend.*, 1904, 139, 215—216).—Samples of coal from the Montrambert mines were found to contain 5 per cent. of calcium carbonate. Combustion of such coal, for the purpose of estimating the carbon, causes the carbonate to dissociate, and, in consequence, the percentage amount of carbon, calculated from the weight of carbon dioxide obtained, is greater than that corresponding with organic carbon. H. M. D.

Analysis of Solid Fuels. E. GOUTAL (*Ann. Chim. anal.*, 1904, 9, 242—246).—The author points out two important sources of error in the calorimetric assay of fuels, namely, the presence of much slate and the use of commercial oxygen containing hydrogen.

Slate may be removed by treating the sample with a heavy liquid composed of 3 vols. of methylene iodide and 1 vol. of benzene. The coal thus freed from slate is washed with benzene and dried. Any error caused by the presence of hydrogen in the oxygen employed may be avoided by passing the latter through a copper tube heated to redness.

L. DE K.

Estimation of Methoxyl Groups. WILHELM KROPATSCHEK (*Monatsh.*, 1904, 25, 583—592. Compare Gregor, Abstr., 1898, ii, 490; Moll van Charente, Abstr., 1902, ii, 434).—The crystalline substance obtained by Moll van Charente from Gregor's absorbent for hydrogen iodide (potassium arsenite) employed in the estimation of methoxyl groups is KI, As_2O_3 . This compound is not formed, and methyl iodide is not retained by this solution if not more than a 2 per cent. solution of potassium arsenite is used.

The error supposed to be due to the carrying over of amorphous phosphorus is caused by the presence of hydrogen phosphide in the hydriodic acid, and can be avoided by using hydriodic acid prepared by boiling iodine with formic acid in a reflux apparatus. Gregor's absorbent retains hydrogen phosphide.

G. Y.

Estimation of Methyl Alcohol in Commercial Formaldehyde. MILAN J. STRITAR (*Zeit. anal. Chem.*, 1904, 43, 401—403).—Commercial formalin is diluted with 20 volumes of water and treated with an excess of ammonia. The mixture is distilled until about half has passed over. The distillate, which contains only traces of formaldehyde, is feebly acidified with acetic acid, and a convenient portion submitted to Zeisel's iodide process. Two samples of commercial formalin showed respectively 16.5 and 15.1 grams of methyl alcohol in 100 c.c.

M. J. S.

Estimation of Methyl Alcohol by the Iodide Process, especially in the Products of the Distillation of Wood. MILAN J. STRITAR and H. ZEIDLER (*Zeit. anal. Chem.*, 1904, 43, 387—400).—Methyl alcohol in dilute aqueous solution can be estimated with the greatest accuracy by Zeisel's iodide process (Abstr., 1886, 493). The only substances occurring in wood-spirit which could interfere with this estimation are allyl alcohol, methyl acetate, methylal, acetaldehyde, formaldehyde, acetone, guaiacol, creosol, and the dimethyl ethers of pyrogallol and its homologues.

Of these, allyl alcohol yields isopropyl iodide and the corresponding amount of silver iodide. Its amount must therefore be determined by the bromine addition method and due allowance made. The amount of formaldehyde in wood-spirit is very small, and its conversion into methyl iodide is so slow compared with the rapid reaction of methyl alcohol that the error it causes may be neglected. Acetaldehyde and acetone yield no volatile iodide, methylal gives 2 molecules of silver

iodide, but no method is known by which a correction can be applied. Methyl acetate also yields silver iodide corresponding with its methoxyl group. A correction may be obtained from the esterification number of the wood-spirit by estimating the ester value. Guaiacol and the other phenol ethers can be eliminated by shaking with animal charcoal. The charcoal absorbs a little methyl alcohol, but this can be recovered by a slight washing.

The method of analysis employed is therefore as follows: of crude wood-spirit, 5 c.c. are diluted to 500 c.c., and 5 c.c. of this mixture are submitted to the iodide process. The weight of silver iodide multiplied by 272.94 gives grams of methyl alcohol per 100 c.c. Of aqueous wood-spirit containing less than 10 per cent. of methyl alcohol, 10 c.c. are diluted to 50 c.c., shaken for $\frac{1}{4}$ hour with 0.5 gram of charcoal, filtered through a small, moistened filter, the charcoal washed, and the filtrate made up to 100 c.c. Of crude pyroligneous acid, 50 c.c. are neutralised with sodium carbonate, made up to 250 c.c., and filtered through an unmoistened paper filter; 100 c.c. are then made strongly alkaline with sodium hydroxide and distilled until 50 c.c. have been collected. Dilute aqueous solutions of methyl alcohol can be distilled without loss. The distillate is treated with charcoal, &c., as above.

M. J. S.

Analysis of a Mixture of Sucrose, Dextrose, and Lævulose. EMIL REMY (*Chem. Centr.*, 1904, 1, 1672; from *Bull. Assoc. Chim. Sucr. & Dist.*, 21, 1902—1906).—Buisson estimates the three sugars by a polarimetric observation before and after inversion and an estimation with Fehling's solution. The process is criticised, and other formulæ are given instead.

L. DE K.

Testing the Stability of Nitrocellulose. E. BERGMANN and ALOYS JUNK (*Zeit. angew. Chem.*, 1904, 9, 982—984, 1018—1023, 1074—1077).—A lengthy and fully illustrated article unsuitable for adequate abstraction. The degree of stability is judged by measuring the nitrogen oxides evolved during two hours' heating at 132°. The method is somewhat interfered with by the presence of sodium or calcium carbonate.

L. DE K.

New Reagents for Aldehydes. MAURICE PRUD'HOMME (*Bull. Soc. Ind. Mulhouse*, 1904, 74, 169—170).—The well-known Schiff's reagent for the detection of aldehydes consists of an acid solution of magenta decolorised by means of sulphurous acid. The author has greatly improved the delicacy of the test by substituting for the sulphite a solution of sodium hyposulphite prepared by the action of zinc dust on sodium hydrogen sulphite.

Another reagent is prepared by decolorising an acid solution of diazomagenta by hyposulphite. The first reagent is valuable for the detection of benzaldehyde, which is scarcely affected by Schiff's reagent. A fine violet colour is obtained.

L. DE K.

Detection of Formalin in Milk. J. EURY (*Ann. Chim. anal.*, 1904, 9, 254).—A modification of Hehner's method, which avoids the charring action of the sulphuric acid.

Five c.c. of milk are mixed with 5 c.c. of dilute sulphuric acid (1:1) and 5 drops of a 1 per cent. solution of ferric chloride and then heated to boiling. If formalin is present, a violet colour appears which persists for about five minutes; the mixture then turns brown. One mg. of formalin may thus be detected in a litre of milk.

L. DE K.

The Iodoform Reaction for Citric Acid. T. C. N. BROEKSMIT (*Chem. Centr.*, 1904, i, 1671; from *Pharm. Weekbl.*, 1904, 41, 401—404).—Citric acid in aqueous solution may be detected by heating with potassium permanganate, adding ammonia, and then tincture of iodine, which causes a precipitate of iodoform. In the presence of other substances it is advisable to precipitate the acid by means of ammonia, barium chloride, and alcohol. The barium citrate, after being washed with alcohol, is then dissolved in boiling dilute acetic acid and identified as described.

L. DE K.

The Orcinol Test for Glycuronic Acid. E. C. VAN LEERSUM (*Beitr. chem. Physiol. Path.*, 1904, 5, 510—512).—Doubt is cast on the trustworthiness of this test.

W. D. H.

Estimation of Fat in Cheese by Gerber's Method. MORITZ SIEGFELD (*Milch-Zeit.*, 1904, 33, 433—435).—Results obtained by various modifications of this method are given. The modifications included the use of different forms of graduated tubes and the substitution of hydrochloric for sulphuric acid as a solvent of the cheese.

Very concordant figures were obtained in all cases. It was found impossible, however, to estimate the fat in highly decomposed cheeses by this method, owing to the formation of a persistent clotted layer between the acid solution and the separated fat.

W. P. S.

Presence of Lecithin in Wine. AUGUSTE ROSENSTIEHL (*Chem. Zeit.*, 1904, 28, 663—664).—A reply to Ortlieb and Weirich (this vol., ii, 304), who maintain that lecithin is the only efficacious constituent of wine. Ortlieb and Weirich detected lecithin in Thyra wine only, but they have not examined ordinary wines for its presence; the conclusions they draw are based on insufficient data. Although lecithin is decomposed on evaporating its concentrated solution, it is quite stable in dilute solution, which may be concentrated by evaporation at 95°.

A. MCK.

General and Physical Chemistry.

Evidence for the Possibility of Resolving an Optically Active Compound without direct Fission and without the Aid of Optically Active Substances. ERNST MOHR (*Ber.*, 1904, 37, 3470. Compare this vol., i, 653).—The priority of Kipping is conceded (compare Kipping and Hall, *Trans.*, 1901, 79, 442; Kipping and Salway, 1904, 85, 438).
J. J. S.

Spectro-analytical Recognition of Argon in Atmospheric Air. EMIL WARBURG [with LILIENFELD] (*Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 1196—1197).—The sensitiveness of ordinary flame reactions is not influenced by the presence of other substances, but it is far otherwise in the case of the emission of light by gases in vacuum tubes. Thus 37 per cent. of argon in nitrogen is scarcely perceptible. The nature of the light emission is, however, greatly dependent on the current, and the author describes an arrangement by which the argon lines can be easily recognised in atmospheric air at 3 mm. pressure.
L. M. J.

Discontinuous Glow Spectra of Solid Organic Substances. EUGEN GOLDSTEIN (*Chem. Centr.*, 1904, ii, 286; from *Verh. Deut. physikal. Ges.*, 3, 156—170. Compare *Abstr.*, 1903, ii, 524).—Many solid aromatic substances, even of those containing only carbon, hydrogen, and oxygen, exhibit a discontinuous spectrum when exposed to the action of the cathode rays at the temperature of liquid air. If the discharge is stopped, there is a discontinuous after-glow spectrum, which is particularly bright for a short time after the removal of the liquid air. Discontinuous spectra are more readily obtained from substances with two or more rings (heterocyclic as well as carbocyclic) than from those with only one ring. Some substances, however, with two or three rings, especially nitro-derivatives, show no discontinuous spectrum.

Replacement of a hydrogen atom by a group consisting of carbon and hydrogen atoms produces little effect; replacement by other elements produces a marked effect on the type of the spectrum. So far as the character of the maxima and their general arrangement is concerned, the spectrum type is the same for position isomerides, although the absolute position, and sometimes the number, of the maxima differs from one isomeride to another. It is noteworthy that mercury lines cannot be detected in the spectrum of mercury diphenyl.

There is no essential difference in these spectrum phenomena at ordinary and at low temperatures, but cooling is to be recommended in order to prevent sublimation and decomposition. The fluorescence exhibited by solutions of many of the substances investigated has nothing to do with the spectra of the solid substances, for the

fluorescence spectra of the solutions are continuous. The absorption spectra do not correspond with the emission spectra, for the phosphorescence of the substances depends on a change brought about by their exposure to the rays. J. C. P.

Emission Spectra of Aromatic Compounds. EUGEN GOLDSTEIN (*Chem. Centr.*, 1904, ii, 286; from *Verh. Deut. physikal. Ges.*, 6, 185—190. Compare previous abstract).—Although a discontinuous spectrum is more readily obtained from substances with two rings in the molecule (phthalic and benzoic acids give a continuous, their anhydrides a discontinuous, spectrum), still there are substances with one ring (hydrocarbons, specially the xylenes, and phenols) which exhibit a discontinuous spectrum, either while they are exposed or afterwards. Benzoic, *p*-hydroxybenzoic, anisic, and terephthalic acids and phenol give primarily a continuous spectrum, whilst that of the afterglow is discontinuous. The colours are different in the two cases; sometimes they appear together, and then the intensity of the one falls off more rapidly than that of the other. The spectrum type is the same for ortho-, meta-, and para-compounds. J. C. P.

Phosphorescent Substances. KARL A. HOFMANN and W. DUCCA (*Ber.*, 1904, 37, 3407—3411. Compare Becquerel, this vol., ii, 6; Tommasina, this vol., ii, 7).—Phosphorescent zinc sulphide is obtained by Henry's method (*Abstr.*, 1893, ii, 72) from commercial zinc chloride, but not from chemically pure zinc ammonium sulphate. If 5 grams of sodium chloride and 0.2—0.5 gram of magnesium chloride are added to 20 grams of pure zinc ammonium sulphate dissolved in 400 c.c. of water, and the precipitate, with hydrogen sulphide, is dried without being washed, the yellow, crystalline zinc sulphide, which remains after heating, is highly phosphorescent. Contrary to Henry's statement, the phosphorescence must be due to the presence of traces of the sodium and magnesium salts. The addition of sodium chloride or of magnesium chloride alone does not cause the phosphorescence. The presence of traces of iron, nickel, cobalt, bismuth, chromium, or copper salts diminishes, but traces of salts of tin, selenium, manganese, or cadmium increase the effect. G. Y.

The Ring system of Benzene. VI. Fluorescence. HUGO KAUFFMANN (*Ber.*, 1904, 37, 2941—2946. Compare *Abstr.*, 1900, i, 480; 1901, i, 318; 1903, i, 19).—Compounds showing violet fluorescence in alcohol or acetic acid solution show a violet luminescence when their vapour is exposed to Tesla-rays. This conclusion is confirmed by the examination of a large number of ring-compounds. The luminescence and fluorescence are found to be increased by the introduction of carbethoxyl groups in the ortho-position.

Ethyl dihydrocollidinedicarboxylate is fluorescent in the solid state or in glacial acetic acid solution, but not in alcohol, ether, or benzene. In this and similar compounds, the violet emission is connected with the presence of parallel double linkings.

Compounds with green fluorescence are not in most cases volatile

without decomposition, and it has not therefore been possible to compare the colour of the luminescence. C. H. D.

Radium Rays and Benzene Derivatives. HUGO KAUFFMANN (*Ber.*, 1904, 37, 2946--2948. Compare preceding abstract).—Solid aromatic compounds were exposed in a thin layer to the action of radium rays. In the majority of cases, fluorescence is produced, this being especially the case with polynuclear compounds and those which become luminescent in vapour under the influence of Tesla-rays. Ethyl dihydrocollidine- and dihydrolutidine-dicarboxylates fluoresce almost as strongly as platinicyanides. Coloured compounds, such as azobenzene, nitroanilines, diphenylaminoquinoxaline, and ethyl *o*-aminocinnamate, do not respond, although the two latter compounds are fluorescent with light. The β -rays appear to be the exciting cause.

C. H. D.

Determination of the Intensity of β -Rays and Some Measurements of their Absorption. WILHELM SEITZ (*Chem. Centr.*, 1904, ii, 581; from *Physikal. Zeit.*, 5, 395—397).—The intensity of β -rays has been determined by measuring the negative charge which an insulated plate suspended in a vacuum received when exposed to the rays. The preparation was placed between mica plates outside the vacuum apparatus, which was closed by aluminium foil. By means of a simple arrangement, the contact between the plate and the electrometer after exposure to the rays could be broken in the vacuum. In measuring absorption, the substance was placed between mica and aluminium foil. It was found that when 7 mg. of Buchler's radium bromide were placed in layers of tinfoil, the absorption-coefficient decreased as the thickness of the layers was increased, because the rays emitted by this substance are not homogeneous. About 0.29 per cent. of the rays pass through lead plates of 3 mm. thickness (compare Paschen, this vol., ii, 461). Lenard's law of the absorption of cathode rays holds approximately. The greater the atomic weight of the substance, the greater the absorption for equal masses per unit surface. Seven mg. of radium bromide yield continuously 5.6×10^{-12} amperes in the form of γ -rays. E. W. W.

Coloration produced by Becquerel Rays. Application to Crystallography; Colorimetric Estimation of Radioactivity. C. J. SALOMONSEN and G. DREYER (*Compt. rend.*, 1904, 139, 533—535).—Plates of quartz exposed to the action of radium salts become strongly coloured. The minute examination of such plates cut perpendicular to the optical axis shows the presence of a system of lines and striæ parallel with the binary axes of the crystal. Adjacent portions of the striated system differ considerably in the intensity of the coloration, and exposure of the quartz to radium thus shows clearly its heterogeneity of structure.

The coloration of glass by Becquerel rays affords a means of quantitative measurement, a scale of standards being easily obtained by exposing the glass to pure radium salt for different times. The sensi-

tiveness of the glass depends on the composition. Jena borosilicate crown glass (No. 3453) was found to be particularly sensitive.

H. M. D.

Becquerel Rays and Water. FRIEDRICH KOHLRAUSCH (*Chem. Centr.*, 1904, ii, 296; from *Verh. Deut. physikal. Ges.*, 5, 261—262).—The conductivity of water exposed to radium rays increases more rapidly than that of water contained in the same vessel, but not similarly exposed. This additional increase of conductivity in the case of the exposed water corresponds with an increase in the ions of about 1/5000th mg. per day. The ions may be produced from the water by the exposure, or the rays may accelerate the solution of the glass. If a current of air is led over the radium salt and then through the water, the latter shows no increase of conductivity. J. C. P.

Action of Radium Emanations on Diamond. Sir WILLIAM CROOKES (*Proc. Roy. Soc.*, 1904, 74, 47—49).—An "off colour" diamond, of a very pale yellow colour, was put inside a tube with radium bromide and, after 78 days, the diamond had darkened and become bluish-green in tint, no yellow colour being apparent. When heated at 50° in a mixture of nitric acid and potassium chlorate for 10 days, the diamond lost its dull surface colour and was bright and transparent, but its tint had changed to a pale bluish-green.

The radium emanations have accordingly a double action on the diamond. The β -rays effect a superficial darkening, converting the surface into graphite in a manner similar to, but less strongly than, the more intense electrons in the cathode stream.

In the presence of radium, the diamond is extremely phosphorescent, and continues to shine during the time of the experiment.

The diamond which had been submitted to the action of radium was still strongly radioactive after it had been away from radium for 35 days, for 10 of which it was being heated in a mixture powerful enough to dissolve its outer skin of graphite. A. McK.

Chemical Actions of Radium. GIOVANNI PELLINI and M. VACCARI (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 269—275).—A glass tube containing 5 mg. of radium bromide and covered with thin aluminium foil was sealed up in an outer glass tube and immersed in various reacting solutions. It was found that after some time the walls of the outer glass tube became coloured violet, the intensity of the coloration being irregularly distributed over the glass.

The author's experiments show that not all the chemical reactions induced by light, even the most sensitive ones, are brought about by the action of radium. Radium seems to favour processes of oxidation, such as that of hydriodic acid. T. H. P.

Chemical Action of Radiations of Short Wave-length on Gaseous Compounds. EMIL WARBURG [with E. REGENER] (*Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 1228—1231).—It has been shown that the silent discharge possesses both ozonising and deozonising action, and experiments were made to measure these actions in the case of

radiations of short wave-length obtained from a spark discharge. As the deozonising action is but little reduced when the discharge occurs in a thin-walled glass tube, the wave-length of the active rays is under 0.3μ . Curves for the ozonising and deozonising action were obtained and indicate an equilibrium at about 2.2 per cent. ozone, but this is dependent on the condition of the quartz vessel employed, that is, on its permeability to the ozonising and deozonising rays. With the same apparatus, ammonia gas was decomposed to the extent of 11 per cent. with but little decrease of velocity. Nitric oxide and nitrous oxide were also decomposed (see Abstr., 1900, ii, 721).

L. M. J.

Chemical Action of the Cathode Rays. EMIL BOSE (*Chem. Centr.*, 1904, ii, 173; from *Physikal. Zeit.*, 5, 329—331. Compare Wiedemann and Schmidt, Abstr., 1898, ii, 291; Schmidt, Abstr., 1902, ii, 237).—When a very strong potassium hydroxide solution (surface = 200 sq. cm.) is exposed in vacuum to the action of a cathode discharge, there are found subsequently in the gaseous phase both hydrogen and oxygen, the volume of the former being considerably more than twice that of the latter. This excess of hydrogen is 10 to 30 times as great as the amount simultaneously produced in a hydrogen voltameter under reduced pressure. The cathode rays, therefore, not only produce an electrochemical effect according to Faraday's laws, but give rise to chemical action in some other way. The most probable source of this is the kinetic energy of the cathode rays, and a computation shows that this is indeed sufficient to produce far greater chemical effects than the electricity carried with the rays, although of course a large proportion of the mechanical energy referred to is doubtless transformed into heat directly. That in the experiments described above such a large excess of hydrogen was obtained is due to the greater solubility of oxygen, and the electrolyte was shown in several cases to retain considerable quantities of that gas.

Generally speaking, the purely chemical action of the cathode rays is electrochemical; those changes such as the coloration of alkali haloids, which have not been shown to be chemical in character or which can be reversed by the heating action of the rays, are probably dissociation effects due to the dynamic action of the rays. This dynamic action will be still greater than the chemical action in the case of the Becquerel rays.

J. C. P.

Phenomena observed in Air Ionised by Radioactive Substances. AUGUSTO RIGHI (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 233—240).—The author describes a sensitive electroscope for comparing the radioactivities of different substances. It consists of a box, the two sides and the top and bottom faces of which are of brass, whilst the two ends are of glass lined with metal gauze. To facilitate the entry of the active rays, the bottom face and one side face are provided with circular windows of thin aluminium. Passing through the top of the box are: (1) a metal rod, carrying at its end a rod of insulating

material (fused quartz, sulphur, or amber), to which is attached a slender gold leaf about 10 mm. wide; (2) a metal wire passing down a glass tube and carrying a strip of silvered copper, which is about 1 mm. wide, and is bent so as nearly to touch the gold leaf. When this wire is in permanent communication with the insulated pole of a dry battery or of a battery of a few accumulators, the gold leaf is attracted to the metal strip and then repulsed. On bringing a radioactive substance near to the instrument, the gold leaf falls and touches the metal strip, is then repelled, falls again, and so on. It is found that the intensity of the radioactivity is inversely proportional to the duration of one of these oscillations. The orientation of the radioactive substance with regard to the apparatus influences considerably the period of oscillation.

T. H. P.

Ionisation of Gases and Vapours caused by Polonium Rays. CACILIA BÖHM-WENDT (*Chem. Centr.*, 1904, ii, 873—874; from *Physikal. Zeit.*, 5, 509—511).—The ionisation caused by the complete absorption of polonium rays (Marckwald's radiotellurium) by various gases has been directly determined for high and low *E.M.F.*, or calculated by extrapolation. In a small vessel in which the absorption is incomplete, the saturation current is dependent on the density of the gas, but with larger vessels in which there is practically total absorption, the ionisation is independent of the nature of the gas, the saturation current being the same in all cases. Air, coal gas, carbon dioxide, and mixtures of air with benzene, toluene, chloroform, or ether have been examined. Ether shows an exceptional behaviour; the current intensity for high *E.M.F.* is constant for the same gaseous mixture, but has an abnormally low value. The *E.M.F.* required for the saturation current increases with lapse of time. The ions first formed possibly act as nuclei for condensation, and become less mobile as their mass increases.

E. W. W.

Radioactive Gas obtained from Crude Petroleum. E. F. BURTON (*Chem. Centr.*, 1904, ii, 874; from *Physikal. Zeit.*, 5, 511—516).—A petroleum from Petrolia, Ontario, which rises from a stratum of calcium carbonate at a depth of about 150 metres, has been found to yield a radioactive gas. A gaseous mixture of sp. gr. 1.05 compared with air was obtained by aspirating air through the hot petroleum. The conductivity of the gaseous mixture increased for about 3 hours, attaining a maximum which was about 40 per cent. greater than its initial value, but in 3.12 days it decreased to about half. The results obtained are practically in accordance with a potential law, the variations with time being independent of the initial potential. In the exponential function $J_t = J_0 e^{-\lambda t}$, the value of $1/\lambda$ increases continuously, probably because the gas contains a trace of a radioactive substance which is more stable than the emanation. The mean values of $1/\lambda$ were found to be approximately equal to those obtained when pure radium compounds were employed. The activity of fresh air which has been passed through the petroleum gradually decreased, but even after a month it had not completely disappeared, the conductivity

being then about 1.6 times the normal value. The petroleum may contain a trace of radium itself. The induced radioactivity decreases in geometrical ratio, falling to half in 35 minutes. E. W. W.

Radioactivity of Soils and Well Sediments. JULIUS ELSTER and HANS GEITEL (*Chem. Centr.*, 1904, ii, 174; from *Physikal. Zeit.*, 5, 321—325).—The radioactivity of numerous samples of the above has been detected and measured. J. C. P.

Mercury Sulphate and Standard Cells. GEORGE A. HULETT (*Zeit. physikal. Chem.*, 1904, 49, 483—501).—It is known that the *E.M.F.* of the Weston cell varies with the method of preparing the mercurous sulphate required. The author has studied the extent of this variation, and recommends an electrolytic method of preparing the sulphate. Sulphuric acid is electrolysed with a platinum cathode and a mercury anode, and the mercurous sulphate formed is prevented by a stirrer from settling on the anode. When this mercurous sulphate is used in the preparation of a Weston cell, the *E.M.F.* is constant from the first, and has exactly the same value in different cells, namely, 1.01908 volts at 21.1°.

By shaking mercuric sulphate and dilute sulphuric acid with mercury for some time, the same equilibrium is reached as when mercurous sulphate alone is used. It is shown that mercuric sulphate is present in the cell, and analysis gives the ratio $\text{Hg}^+/\text{Hg}^{++}=40$, a much smaller value than that found by Abel (*Abstr.*, 1901, ii, 376). The experiments indicate that mercurous sulphate is affected by the cadmium sulphate solution, and accordingly the hydrolysis of the former salt has been studied in detail. After prolonged shaking with mercury and water, the water being renewed at intervals, the residue has an exceedingly small solubility, and analysis indicates that the compound HgHSO_4 has been slowly removed and that the residue consists of a basic salt, thus: $3\text{Hg}_2\text{SO}_4 + 2\text{H}_2\text{O} \rightleftharpoons (\text{HgOH})_2, \text{Hg}_2\text{SO}_4 + 2\text{HgHSO}_4$ (compare Gouy, *Abstr.*, 1900, ii, 481). If this basic salt is substituted for pure mercurous sulphate as the depolariser in a Weston cell, the *E.M.F.* is considerably greater than the value given above. The author has determined also the solubility of mercurous sulphate in sulphuric acid solutions of various concentration, and finds a marked discontinuity at the concentration $v=1$. This indicates that the mercurous sulphate used in the standard cells should be prepared from sulphuric acid of greater concentration than that just referred to.

It is shown in the paper that mercurous salts may conveniently be estimated as chloride by precipitating with a slight excess of a dilute chloride solution and drying the mercurous chloride obtained in a vacuum desiccator for 12—24 hours. J. C. P.

[Standard Cells.] NORMAN T. M. WILSMORE (*Zeit. Elektrochem.*, 1904, 10, 685).—To prevent the glass breaking at the point at which the platinum wire making contact with the zinc or cadmium amalgam is sealed through it, the author places the platinum wire at the end of a short, narrow tube, which is filled with asbestos, so that the amalgam

does not come in contact with the platinum close to the place at which it passes through the glass. Figures are given of two convenient forms of mercury electrodes. The improvement consists in using a two-way tap, of the kind used on gas pipettes, instead of the usual plain syphon for connecting the electrode to other electrodes.

T. E.

The Carbon Cell. FRITZ HABER and LUDWIK BRUNER (*Zeit. Elektrochem.*, 1904, 10, 697—713).—Carbon and iron immersed in fused sodium hydroxide give a difference of potential of about a volt, the current flowing from carbon to iron in the electrolyte. The chemistry of the cell is not definitely known. Iron immersed in fused sodium hydroxide is at first rapidly dissolved. In some circumstances, however, it becomes passive. If the iron is immersed in fused sodium nitrate, it is covered with a dark skin of oxide, which is difficult to remove; such iron is passive. Addition of manganate to the sodium hydroxide also produces the passive condition, and the more readily the less water the sodium hydroxide contains. This is explained by the fact that dry sodium hydroxide does not yield any hydrogen when electrolysed, and therefore, since no hydrogen can be evolved at the surface of the iron, the skin of oxide is formed more completely. Since all sodium hydroxide, especially when fused in contact with iron and air, contains more or less manganate, it appears that iron protected by a skin of oxide and immersed in sodium hydroxide containing manganate is really an oxygen electrode, the part played by the manganate being that of an intermediary, by means of which the atmospheric oxygen can pass into the ionic condition.

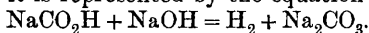
In order to measure the potential of the iron and carbon electrodes in fused sodium hydroxide, the standard *N/10* calomel electrode was connected to the fused electrolyte by a stick of solid sodium hydroxide, one end of which touched the fused electrolyte, the other end being attached to the syphon of the calomel electrode by a piece of rubber tubing. The end of the syphon in direct connection with the stick of sodium hydroxide was filled with gypsum soaked in sodium hydroxide solution. The *E.M.F.* of the combination, passive iron in sodium hydroxide | calomel electrode, was found to be -0.265 volt at 312° , increasing to -0.472 volt at 532° . This *E.M.F.* is independent of the quantity of manganate in the electrolyte if this is not very small or very large.

The *E.M.F.* of the combination, carbon in fused sodium hydroxide | calomel electrode, varies very much with the nature of the carbon employed, -0.66 volt being found with artificial graphite and -1.4 volts with a partially disintegrated arc-lamp carbon. The carbon is attacked by fused sodium hydroxide, hydrogen being evolved. The more rapid the evolution of hydrogen, the greater is the *E.M.F.* When a very rapid evolution of hydrogen is produced by heating the sodium hydroxide to 500° , the *E.M.F.* rises to -1.5 volts. When a platinum tube through which a current of hydrogen is passed is substituted for the carbon electrode, the same *E.M.F.* is observed, namely, -1.48 to -1.5 volts. It appears therefore that the carbon electrode is really a hydrogen electrode. That *E.M.F.*s lower than -1.5 volts

are often observed is readily explained by the partial depolarisation of the electrode by the manganate present in the electrolyte. It is only when the temperature is sufficiently high to produce a rapid evolution of hydrogen that the full value is observed. When the carbon is once charged with hydrogen, however, it retains the high *E.M.F.* for some time at lower temperatures.

The possibility that, by the action of atmospheric oxygen, the carbon may first be oxidised to carbon monoxide, and that this may react with sodium hydroxide to form formate or oxalate, is also considered.

It is shown that carbon and sodium hydroxide react, giving pure hydrogen. Sodium formate and sodium hydroxide, when fused together, give off pure hydrogen, the reaction begins at about 205° and is quite complete at 350°; it is represented by the equation



No oxalate is formed. A mixture of sodium oxalate and sodium hydroxide begins to decompose at 270—280°, evolving pure hydrogen and forming carbonate only. If the potential of the carbon electrode were due to the presence of either formate or oxalate, it should be higher than the hydrogen potential, because both formate and oxalate break up spontaneously yielding hydrogen. Measurements of the potential of carbon in sodium hydroxide to which formate or oxalate had been added, and from which hydrogen was being evolved owing to their decomposition, always gave the hydrogen potential -1.5 volts. The action of carbon monoxide on sodium hydroxide at 350° was found to be $2\text{NaOH} + \text{CO} = \text{Na}_2\text{CO}_3 + \text{H}_2$.

It is therefore proved that the carbon electrode is really a hydrogen electrode, the hydrogen being formed by the action of carbon on sodium hydroxide, and the reaction to which the *E.M.F.* of the cell is due is the formation of water from this hydrogen and atmospheric oxygen.

The *E.M.F.* of the cell agrees well with the *E.M.F.* required to decompose into hydrogen and oxygen the small quantities of water dissolved in fused sodium hydroxide. The application of Helmholtz's formula to the results leads to the conclusion that the vapour pressure of this dissolved water must be extremely small, but the values calculated are much affected by small experimental errors. T. E.

A Simple Standard Electrode. H. DANNEEL (*Zeit. Elektrochem.*, 1904, 10, 685).—A mercury electrode with a simple arrangement for filling and rinsing out the syphon. T. E.

Behaviour of Unattackable Anodes in the Electrolysis of Hydrochloric Acid. EMIL BOSE (*Zeit. physikal. Chem.*, 1904, 49, 227—228).—Many of the points raised in Luther and Brislee's paper (*Abstr.*, 1903, ii, 708) have already been dealt with by the author (*Abstr.*, 1899, ii, 348). J. C. P.

Anodic Evolution of Oxygen. FRITZ FOERSTER and A. PIGUET (*Zeit. Elektrochem.*, 1904, 10, 714—721).—Smooth matt and platinised platinum, smooth iridium, palladium, nickel and iron electrodes were used as anodes in potassium hydroxide solution. The current was

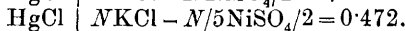
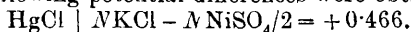
kept constant at 0.033 ampere per. sq. cm. and the *E.M.F.* measured from time to time. The cathode being of platinised platinum, the whole of the change of *E.M.F.* takes place at the anode. In every case, the *E.M.F.* rises more or less rapidly, finally attaining a constant value which is different for each electrode. The platinum metals gave the same result in sulphuric acid. The differences observed are similar to those found with currents which are just capable of producing a visible evolution of gas, but are much larger. The authors incline to the hypothesis that they are due to the formation of a thin layer of absorbed gas on the surface of the electrode. T. E.

Electrolytic Separation from their Salt Solutions of Metals which decompose Water. A. SIEMENS (*Zeit. anorg. Chem.*, 1904, 41, 249—275).—A metal which decomposes water can be separated electrolytically from the aqueous solution of one of its salts either if the supertension of hydrogen towards it is considerable or if it can be depolarised. In the first case, the Nernst formula, $RT/n \log C_M c_M = RT \log C_H / c_H + \eta$, is applicable; if the value for the left side of the equation is smaller than, or equal to, that for the right side, the metal will separate, whilst if it is greater, hydrogen will separate. With metals of higher supertension than zinc, the value for the right side of the equation is always greater than that for the left; those metals may, however, separate if a suitable depolariser be used, and in this case this equation becomes $RT/n \log C_M c_M - \theta = RT \log C_H / c_H + \eta$, where θ represents the value of the depolarisation. In this way, metals of the alkalis or alkaline earths may be separated from their aqueous solutions when mercury is the cathode.

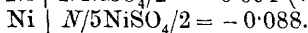
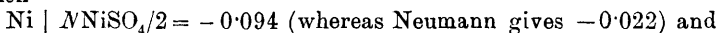
Magnesium separates along with nickel when solutions of mixtures of magnesium sulphate and nickel sulphate are electrolysed, the anode being nickel and the cathode platinum, only, however, when the concentration of the magnesium salt in the electrolyte is high. When the concentration of the magnesium salt is low, and especially when an ammonium salt is present, a quantitative electrolytic separation of magnesium from nickel is possible. The influence of concentration, temperature, and current density on the separation of nickel, together with magnesium, was investigated. Similarly, magnesium can be electrolytically separated along with cobalt, to a less extent with iron, and very slightly with zinc. Aluminium and metals of the alkaline earths cannot be separated, together with heavy metals, from aqueous solutions. Alkali metals separate in traces, along with nickel and tin, from aqueous solutions, but not along with iron and silver. No alloys of definite composition were in any case obtained, the heavy metal simply serving as solvent for the light metal. The high potentials of the precipitates deposited from mixed salt solutions are a proof of the presence of the light metals.

Nickel magnesium sulphate in aqueous solution does not form complex ions; it differs in this respect from nickel ammonium sulphate. Salts of the alkalis and alkaline earths in acetone solution are reduced to the corresponding metals, but this is not the case with salts of magnesium, aluminium, and glucinum. A. McK.

Electric Potential of Nickel and Tellurium. HANS EULER (*Zeit. anorg. Chem.*, 1904, 41, 93—96).—In the electrometric investigation of complex nickel salts, it is necessary to use nickel electrodes, which exhibit a constant potential towards nickel salts; the best electrodes were found to be those with a rough-grained surface. They are treated first with dilute sulphuric acid and then immersed in a $N/1$ nickel sulphate solution, being made alternately the anode and the cathode. When they are agitated for 4 days with $N/1$ nickel sulphate, they act as well as the best electrodes of the first order. The following potential differences were obtained:



If the potential of the calomel electrode be taken as $= 0.560$ volt, then



The following potential difference was obtained with tellurium electrodes.

Te \mid saturated solution of telluric acid $- \text{NKCl}, \text{HgCl} = -0.00$ volt. With other specimens, both higher and lower values were obtained.

A. MCK.

Determination of a Transference Number in the Electrolysis of a Fused Salt. RICHARD LORENZ and G. FAUSTI (*Zeit. Elektrochem.*, 1904, 10, 630—633).—A fused mixture of potassium and lead chlorides is used. Two small porous cells immersed in the fused salt form the anode and cathode compartments. The weight and composition of the salt contained in the cathode cell, and also the quantity of lead produced and the quantity of electricity passed, are determined. In every case it is found that the cathode liquid loses more lead than is deposited, hence the lead must be present in the fused electrolyte (at about 800°) in the form of a complex anion. With a mixture of equal molecules of potassium and lead chlorides, the value of the transference number for potassium found was about 0.3, but the results are very uncertain on account of the great experimental difficulties.

T. E.

Conductivity of Solutions of Sodium in Absolute Alcohols, in Alcohols diluted with Water, and in Mixtures of Two Alcohols. S. TIJMSMA (*Zeit. physikal. Chem.*, 1904, 49, 345—367).—The investigation, of which a preliminary notice has appeared (*Abstr.*, 1903, ii, 628), has been continued. Solutions of sodium in absolute methyl alcohol conduct better than those in absolute ethyl alcohol, and the latter better than those in absolute propyl alcohol. The limiting value of the molecular conductivity cannot be actually determined in any of the three cases, neither can it be calculated by Ostwald's dilution law. Solutions in absolute propyl alcohol exhibit the peculiarity that the difference between successive values of the conductivity becomes greater as the dilution increases, owing probably to the great viscosity of the concentrated solutions. The conductivity of solutions in mixtures of ethyl and methyl alcohols, or in mixtures

of methyl and propyl alcohols, can be calculated from the conductivities in the separate alcohols. The addition of water to solutions in ethyl alcohol increases the conductivity at all dilutions, whilst with methyl alcohol this is the case only with concentrated solutions; in the more dilute solutions, addition of water first diminishes the conductivity and then increases it, if in sufficient quantity. This is probably due to the migration velocity of the OCH_3 ion in methyl alcohol being greater than that of the OH ion. J. C. P.

Conductivity of Solutions of Radium Bromide. FRIEDRICH KOHLRAUSCH and FRITZ HENNING (*Chem. Centr.*, 1904, ii, 296; from *Verh. Deut. physikal. Ges.*, 6, 144—146).—The specific conductivity of solutions of radium bromide has been determined at 18° , and the molecular conductivity has been calculated, the atomic weight being taken as 225. The value of Λ_∞ is about 125, and the ionic conductivity of $\frac{1}{2}\text{Ra}$ is 57, comparable with that of $\frac{1}{2}\text{Ba}$, which is 56. The temperature-coefficient for the radium ion in water is 0.024 in the neighbourhood of 18° . If Runge and Precht's value for the atomic weight is taken, namely, 258, then $\Lambda_\infty = 135$, and the ionic conductivity of radium is 67. The behaviour of radium bromide, with its very high molecular weight, is a fresh example of the fact that the atomic weight is not an important factor in determining the behaviour of a salt towards water. J. C. P.

Conductivity of Aqueous Solutions of Electrolytes with Bivalent Ions. FRIEDRICH KOHLRAUSCH and E. GRÜNEISEN (*Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 1215—1222).—The electrical conductivity was determined at concentrations varying from 0.0001*N* to *N* in the case of solutions of the chlorides of barium, magnesium, and calcium; nitrates of barium, strontium, calcium, and lead; the sulphates of potassium and lithium, and potassium oxalate. The values obtained are compared with those calculated by the equation $(L_0 - L)/L^p = c.m^{\frac{1}{2}}$, where L and L_0 are the conductivities at the concentration m and infinite dilution, p and c being constants. The observed and calculated values agree well between the concentrations 0.0005*N* and 0.2*N*. For high dilutions, however, the calculated values are considerably too high. The migration velocities are calculated as $\frac{1}{2}\text{Ba}$, 55.9; $\frac{1}{2}\text{Sr}$, 51.9; $\frac{1}{2}\text{Ca}$, 52.1; $\frac{1}{2}\text{Mg}$, 46.1; $\frac{1}{2}\text{Pb}$, 61.5; $\frac{1}{2}\text{SO}_4$, 68.7; $\frac{1}{2}\text{C}_2\text{O}_4$, 63.8. The conductivities of the sulphates of magnesium, zinc, cadmium, and copper, of calcium chromate, and of magnesium oxalate were also determined. The equation previously employed is not available, but at dilute solutions the results are in accord with those obtained from the equation $L_0 - L = P.m^{\frac{1}{2}}$, where P is a constant. This signifies that the difference between the conductivity and its limiting value is proportional to the square root of the concentration, or, if L/L_0 be regarded as the electrolytic dissociation, that the difference between the dissociation and unity is proportional to the square root of the concentration, and it is shown that the various values for L_0 recalculated by this expression are in good accord. The migration velocities are also calculated, and are about 1 per cent. less than those previously obtained. L. M. J.

Dissociation of Electrolytes in Alcoholic Solutions. T. GODLEWSKI (*Bull. Acad. Sci. Cracow*, 1904, 6, 239—276. Compare Abstr., 1893, ii, 257; 1898, ii, 154).—The numbers obtained for the electrical conductivity of eight organic acids in ethyl alcohol solution at 18° and at dilutions varying from 8 to 1024 litres are found to satisfy the dilution law. On account of the very feeble dissociation of the acids in ethyl alcohol, the dilution law assumes the simpler form $\mu^2/v = k\mu_\infty^2$. On account of the uncertainty attaching to the absolute values of μ_∞ , the values of the dissociation constant k are not sufficiently well established, and, for the purpose of comparing the different acids, the values of $k\mu_\infty^2$ are taken and compared with the corresponding numbers for the acids in aqueous solution at 25°.

| | Cyanoacetic. | Phthallic. | Malonic. | Bromoacetic. | o-Nitrobenzoic. | Chloroacetic. | Salicylic. | Acetic. |
|--|--------------|------------|----------|--------------|-----------------|---------------|------------|---------|
| Ethyl alcohol, $k\mu_\infty^2 \cdot 10^4 \dots$ | 11.6 | 9.49 | 7.96 | 3.35 | 3.10 | 2.66 | 2.66 | [0.043] |
| Water, $k\mu_\infty^2 \dots$ | 888 | 538 | 235 | 231 | 200 | 172 | 151 | 2.7 |

The relative values of the dissociation constants of the acids differ considerably in the two solvents. The two dibasic acids are especially notable in this respect.

The conductivities of potassium iodide, potassium chloride, sodium chloride, hydrochloric acid, sodium salicylate, and sodium cyanoacetate have been measured in aqueous alcoholic solutions containing the components in all proportions, and values for the maximum molecular conductivities have been deduced. The curves representing the dependence of μ_∞ on the composition of the solvent show a minimum when the solvent contains 70—80 per cent. by volume of alcohol. From the values of μ_∞ and the transport numbers (calculated from that of iodine in potassium iodide and sodium in sodium chloride), the migration velocities of the ions in the various aqueous alcoholic solutions are calculated:

Migration Velocities (18°).

| Vol. per cent. EtOH. | I'. | K'. | Cl'. | Na'. | H'. | OH·C ₆ H ₄ ·CO ₂ '. | CN·CH ₃ ·CO ₂ '. |
|-------------------------|------|------|------|------|-------|--|--|
| 0 | 66.7 | 65.3 | 65.9 | 44.4 | 318.0 | — | — |
| 20 | 37.9 | 36.5 | 38.2 | 27.1 | 188.7 | 17.5 | 21.3 |
| 40 | 24.6 | 23.6 | 26.2 | 19.2 | 120.1 | 12.9 | 15.8 |
| 60 | 20.7 | 19.8 | 20.1 | 15.2 | 75.9 | 11.3 | 14.0 |
| 80 | 19.1 | 18.4 | 17.1 | 14.0 | 50.2 | 11.3 | 14.0 |
| 100 | 27.5 | 21.5 | 23.8 | 14.5 | 32.1 | 12.6 | 15.0 |

These data have been utilised for the purpose of deducing the dissociation of salicylic, cyanoacetic, and bromoacetic acids in aqueous alcoholic solutions. The three acids are found to satisfy the dilution law, whatever the composition of the alcohol water mixture. The dissociation constants $k \cdot 10^5$ are:

Vol. per cent.

| | | | | | | |
|-----------------|-----|-----|-----|------|------|-------|
| EtOH | 0. | 20. | 40. | 60. | 80. | 100. |
| Salicylic | 100 | 83 | 32 | 11 | 1.8 | 0.013 |
| Cyanoacetic ... | 370 | 210 | 120 | 57.3 | 10.7 | 0.05 |
| Bromoacetic ... | 138 | 85 | 35 | 10.2 | 1.7 | 0.015 |

The values of k decrease with increase in the proportion of alcohol, slowly at first, then more rapidly, until the values for pure alcohol are only about 1/30th of those for 90 per cent. alcohol.

The molecular conductivity of acetic acid in amyl alcohol passes through a minimum value at a concentration of approximately 0.5 mol. per litre. This peculiarity cannot be explained by a change in the dielectric constant.

H. M. D.

Ionisation of Chromophores. HERMAN DECKER (*Ber.*, 1904, 37, 2938—2941. Compare Abstr., 1891, 1247; Gadomska and Decker, Abstr., 1903, i, 692).—Quinquevalent nitrogen and quadrivalent oxygen and sulphur, when forming part of an aromatic ring, form chromophoric groups with bromine or iodine. Thus pyridinium and quinolinium methiodides are strongly coloured. When dissociation takes place in solution, the colour disappears, the chlorine and bromine ions being colourless. Thus 6:8-dinitroquinolinium methiodide forms blackish-red needles, but dissolves in water to a colourless solution. The degree of dissociation may in many cases be followed colorimetrically. The chromophoric properties of the acridinium, xanthonium, and thioxanthonium compounds are very strongly marked. In these cases, the dark-coloured bromides and iodides form yellow or orange solutions, the organic ion being itself coloured.

C. H. D.

Magnetisation of the Alkali Metals. ARCIERO BERNINI (*Nuovo Cimento*, 1904, [v], 7, 441—447).—By means of a modified torsion balance similar to that used by Curie and Chénevau (*J. Phys.*, 1903, 2), the author has measured the coefficients of magnetisation of sodium, potassium, and lithium. The values obtained are respectively: $0.5438.10^{-6}$, $0.632.10^{-6}$, and $0.3836.10^{-5}$. These coefficients diminish with temperature and do not undergo a sudden change with a change of state. The values given show that the alkali metals are paramagnetic and not diamagnetic as supposed by Faraday.

W. A. D.

Specific Heat of Superheated Steam. H. LORENZ (*Chem. Centr.*, 1904, ii, 393—394; from *Physikal. Zeit.*, 5, 383—385).—The specific heat of steam between 205° and 340° has been determined by means of a calorimeter through which the steam was passed. Only half the Joule-Thomson effect was taken into account in the calculation of the constant. The results may be approximately represented by the formula $cp = 0.43 + 3,600,000 p/T^3$, in which p is the mean pressure of the steam and T its mean absolute temperature. The formula allows of extrapolation to +172°, and at this temperature gives a value = 0.47; Regnault found by experiment 0.48.

E. W. W.

Heat of Neutralisation of Some Pseudo-acids (isoNitroso-compounds). PAUL TH. MULLER and ED. BAUER (*J. Chim. Phys.*, 1904, 2, 457—471).—The authors have determined the heats of

neutralisation of isonitrosocynoacetic acid and its methyl and ethyl derivatives as well as of ethyl isonitrosoacetoacetate. The results indicate that in the free acid the carboxylic group functionates as a true acid, but that the isonitroso-groups possess a negative heat of dissociation of about 4 cal., which is a characteristic property of the pseudo-acid groups. L. M. J.

Determination of the Heat of Dissociation of Some *iso*Nitroso-acids (Pseudo-acids) by the Conductivity Method. PAUL TH. MULLER and ED. BAUER (*J. Chim. Phys.*, 1902, 2, 472—497).—The dissociation constant can be calculated from the conductivity of a salt or acid, and from the temperature coefficient of this constant the heat of dissociation is readily calculated by the well known Van't Hoff expression. The authors have in this way determined the heats of dissociation of the acids investigated previously (preceding abstract), and it was found that the results thus obtained are in good accord with those obtained from the heats of neutralisation. L. M. J.

Pyrogenic Reactions and Dissociation. WALTHER LÖB (*Zeit. Elektrochem.*, 1904, 10, 504—508).—From his previous experiments (Abstr., 1903, i, 20, 29, 806) the author draws the conclusion that the pyrogenic reactions are most readily understood by assuming that the substances first dissociate and that the products then recombine. He then proceeds to extend this view of chemical change to all reactions, and particularly to the conversion of optical isomerides into each other. Electrolytic dissociation is regarded as a special case of the general dissociation postulated, distinguished by the combination of the products of dissociation with electrons, whereby the reactivity of the products is diminished to such an extent that they can exist in finite concentrations.

The products of dissociation are regarded as compounds in which the valency of the element in question is less than its maximum value. The valency of an element is a function of the experimental conditions. T. E.

Vapour Pressure of Mercury at Ordinary Temperatures. EDWARD W. MORLEY (*Zeit. physikal. Chem.*, 1904, 49, 95—100).—A current of a dry indifferent gas, such as carbon dioxide, was saturated with mercury vapour by passing it for about 14 days through a weighed quantity of the metal contained in an absorption vessel, and the vapour pressure was then calculated from the volume of the gas and the loss of weight of the absorption apparatus. The values of the vapour pressure thus obtained are shown below :

| Temperature. | Vapour pressure in mm. |
|--------------|------------------------|
| 16° | 0.0010 |
| 30 | 0.0027 |
| 40 | 0.0052 |
| 50 | 0.0113 |
| 60 | 0.0214 |
| 70 | 0.0404 |

These values are in good agreement with those given by the formula $p = ab^t$, in which $\log a = 4.6064$ and $\log b = 0.02856$. J. C. P.

A Differential "Araeopcnometer." H. REBENSTORFF (*Chem. Zeit.*, 1904, 28, 889—890).—A combination of a hydrometer and a specific gravity bottle. When filled with the liquid to be tested and placed in water at 15°, the specific gravity may be at once read off on the stem, which is graduated from 1.9 to 2. When the sp. gr. is lower than 1.9, weights are suspended from the bottom of the apparatus until a reading becomes possible and the amount is deducted from the figure on the stem. L. DE K.

Significance of Changing Atomic Volume. IV. Effects of Chemical and Cohesive Internal Pressure. THEODORE W. RICHARDS (*Zeit. physikal. Chem.*, 1904, 49, 15—40. Compare Abstr., 1902, ii, 305; 1903, ii, 132).—The author's conclusions, based partly on some fresh experimental data (see Richards and Stull, this vol., ii, 384), are summarised as follows: Among compounds of lithium, sodium, potassium, chlorine, bromine, and iodine, the compound of a more compressible element is invariably formed with a greater decrease of volume than the compound of a less compressible element, other conditions being equal. Available data for silver chloride, zinc and cadmium chlorides and bromides, and carbon disulphide show that the more volatile the substance (that is, the slighter its cohesive attraction) the greater is the molecular volume, other conditions being equal. A given change in chemical energy produces a smaller change of volume than does the same change of cohesive energy. These facts are explained by the assumption that both chemical energy and cohesive energy exert a compressing effect on a solid or liquid substance, and that the chemically tied part of each atom is more compressed than that which is subject only to cohesive pressure. Polymerisation and crystallisation may cause irregularities, but in the cases of water and tin, which are discussed in detail, there is nothing contradictory to the above explanation. The explanation covers also the relations of density, compressibility, and boiling point exhibited by many isomeric organic compounds. Thus is shown the reason why additive molecular volumes are obtained only when, of two liquids, the less volatile (that is, the more cohesive) is heated to a higher temperature. These varying intensities of internal pressure are regarded as capable of explaining the variety of physical properties, such as tenacity and malleability. The foregoing considerations are regarded as affording increased evidence as to the significance of changing atomic volume, and increased support for the theory of compressible atoms.

J. C. P.

Determination of the Surface Tension and Molecular Weight of Liquid Nitrous Oxide. LEO GRUNMACH (*Sitzungsber. k. Akad. Wiss. Berlin*, 1904, 1198—1202).—The surface tension of liquid nitrous oxide was determined by the capillary wave method previously used for liquid air (Abstr., 1901, ii, 646). The value obtained at 89.3° was 26.323 dynes/cm. The critical temperature of

nitrous oxide is 36.4° (Cailletet and Mathias) or 35.4° (Dewar). The values for the molecular weight calculated from these temperatures and from the surface tension are respectively 43.26 and 43.78, so that the compound has the same molecular weight in the liquid and gaseous states.

L. M. J.

Surface Tension Effects in Beer and in connection with the Preparation of Beer. FRITZ EMSLANDER and HERBERT FREUNDLICH (*Zeit. physikal. Chem.*, 1904, 49, 317—328).—Electrical convection experiments show that beer contains a positive colloid. The colouring matter of beer is largely colloidal in nature, for it also travels to the cathode and is deposited there along with the other colloids. The greater or less permanence of beer froth is connected with its content of colloidal substances (compare Zawidzki, *Abstr.*, 1903, ii, 281; Benson, *ibid.*, 715; Ramsden, this vol., ii, 323). The excess of carbon dioxide held in solution by beer is attributed to absorption by the dissolved colloids, for it has been shown that positive colloids absorb acids. Heat is developed when colloids absorb water and "swell," and the heat given out at many stages in the brewing process is probably due to a similar "swelling." The authors discuss also the bearing of different vessel surfaces on the stability of a super-saturated gas solution.

J. C. P.

Liquefaction of Gaseous Mixtures. F. CAUBET (*Zeit. physikal. Chem.*, 1904, 49, 101—116. Compare *Abstr.*, 1902, ii, 382).—The behaviour of mixtures of carbon dioxide and nitrous oxide has been studied in the manner previously described. The results obtained are somewhat complex and do not lend themselves to abstraction.

J. C. P.

The Most Probable Value of the Gas Constant R . DANIEL BERTHELOT (*Zeit. Elektrochem.*, 1904, 10, 621—629).—The value of R in the equation $pv = RT$ can be obtained from observations on real gases if p is taken small enough. For the permanent gases, the curves representing pv as a function of p (at constant temperature) are straight lines up to 5 or 6 atmospheres. It is therefore possible to calculate the value of pv for $p = 0$ with great accuracy. The data required are the molecular weight of the gas, the weight of a litre of the gas under standard conditions, and the compressibility of the gas between 0 and 1 atmosphere. From the results obtained for seven gases by Leduc and Sacerdote, and using the atomic weights of the International Commission, the volume occupied by 1 mol. of a perfect gas under standard conditions is found to be 22.4135 litres, and, using Lord Rayleigh's measurements on three gases, 22.4098. A rather better agreement is obtained when the more accurate atomic weights $H = 1.0076$ and $C = 12.004$ are used, the numbers becoming 22.4130 and 22.4116 respectively.

Gases containing nitrogen give considerably higher values when Stas' atomic weight (14.04) is used, but taking $N = 14.005$, the normal value is found. The author considers that the atomic weight 14.04 is certainly too high. In order to calculate the value of R , the melting

point of ice on the absolute scale is required. From Joule and Thomson's results, combined with the accurate measurements of the coefficients of expansion of hydrogen, air, and carbon dioxide made by Chappuis, the mean value $T_0 = 273.10$ is obtained. From Chappuis' measurements of the coefficients of expansion and of compressibility of nitrogen and of hydrogen the value 273.08 is calculated. The mean of these two numbers is taken and leads to the final value, $R = 22.412/273.09 = 0.08207$, the units being the atmosphere and litre.

The uncertainty of this number is about one unit in the last place.

T. E.

Numerical Values of Some Important Physicochemical Constants. WALTHER NERNST (*Zeit. Elektrochem.*, 1904, 10, 629—630).—Using the values found by Berthelot in the preceding abstract, the following values are calculated and offered for criticism: $R = 0.83155 \times 10^8$ [Erg. T^{-1}] or $R = 1.98507$ [gram calories T^{-1}]. The latter value is calculated taking the mechanical equivalent of heat as 41.89×10^6 Erg. for the 15° gram calorie. Since 1 watt = 0.23872 gram cal., $R = 0.86134.10^{-4}$ [Watt].

Finally, the molecular weight of an ideal gas is 28.979Δ , where Δ is its density referred to air as unity.

T. E.

More Exact Equation of Condition for Gases. II. J. B. GOEBEL (*Zeit. physikal. Chem.*, 1904, 49, 129—161).—A more detailed mathematical study of the assumptions underlying the equation previously deduced (this vol., ii, 311).

J. C. P.

An Application of Cailletet and Mathias' Method for the Determination of the Critical Volume. MIECYSŁAW CENTNERSZWER (*Zeit. physikal. Chem.*, 1904, 49, 199—207).—Tubes of equal dimensions are filled to different degrees with the liquid under investigation, and after expulsion of air are sealed off. When the ratio of the weight of liquid to the volume of the tube is less than the critical density, the liquid disappears at a certain temperature which can be easily determined, and at this point the mean density of the contents of the tube is the density of the saturated vapour. When the above ratio is greater than the critical density, the vapour will disappear at a certain temperature, and the mean density of the contents of the tube at that point is the density of the liquid under the pressure of its own vapour. From a number of points determined in this way, the density-temperature curve can be constructed and an application of the law of the rectilinear diameter gives the critical volume. In order to test the method, the following critical constants have been determined:

| | Crit. temp. | Crit. dens. |
|----------------------|-------------|-------------|
| Methyl chloride..... | 143.0° | 0.370 |
| Ether | 194.4 | 0.258 |
| Methyl alcohol | 240.2 | 0.275 |

J. C. P.

The Tonometric and Cryoscopic Formulæ. E. ARIÈS (*Compt. rend.*, 1904, 139, 462—464).—From the expression $h_0 = H_0 - x_1 RT$, where h_0 and H_0 represent the potential of the dissolved substance and the solvent respectively and x_1 represents the molecular proportion of the substance dissolved in the molecular weight of the solvent (compare this vol., ii, 648), the author deduces the formulæ used in tonometry and cryoscopy. M. A. W.

A Theory of Solutions. ISIDOR TRAUBE (*Phil. Mag.*, 1904, [vi], 8, 158—165).—The author urges various objections to the accepted theory of solutions; the most important of these are the failure of theory to interpret the case of strong solutions and the discrepancies obtained for non-aqueous solutions. The calculation of the dissociation coefficient may be allowed, but the interpretation of it rejected. An endeavour is made to combine with Arrhenius's theory some of the earlier assumptions of Clausius; this is done by assuming that the molecule or ion of the solute is combined with a molecule of the solvent, and in the state of a dynamic equilibrium, that is, wandering from one molecule to another. It has been shown that the fundamental osmotic laws may be explained by these considerations (Poynting, *Phil. Mag.*, 1896, 42, 289). They also afford an explanation of the influence of association of the solvent on the dissociation of the solute, as it may be assumed that the molecules or ions of the latter are able to dissociate the associated molecules of the solvent and to join with them. In order to obtain definite support for these considerations, the author shows that the well-known equation of Rudolphi and van't Hoff, applicable to strong electrolytes, may be deduced from them (Abstr., 1903, ii, 63). L. M. J.

Critical Point of Dilute Saline Solutions. LEONE LEVI-BIANCHINI (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 174—176).—The author has investigated the critical phenomena of saline solutions, in which the dissolved substance has a negligible vapour pressure, while the ionisation is virtually zero (Walden and Centnerszwer, Abstr., 1902, ii, 245).

With dilute solutions of lithium chloride, bromide, and iodide, and of sodium and potassium bromides and iodides in methyl alcohol, there is perfect homogeneity at the critical temperature and beyond it; the critical temperature is raised proportionately to the concentration. With the chlorides of sodium, potassium, and strontium, the solubility vanishes below the critical temperature of the alcohol. Barium and calcium chlorides seem to undergo alteration and exhibit complex phenomena which recall that of the retrograde condensation of liquid mixtures. Zinc, cadmium, and ferrous chlorides and potassium thiocyanate also decompose, these salts being capable of bringing about various reactions with organic substances. Cobalt chloride remains dissolved in the compressed vapour of the alcohol above the critical temperature, but a gradual decomposition of the chloride takes place with formation of a white, insoluble deposit; on making repeated experiments with the same tube, it is found that the solution becomes almost colourless, while the critical temperature falls to approximately

that of the pure solvent. The cobalt chloride solution gives a colourless vapour over the blue solution at temperatures below the critical point, but when the latter is reached, the whole contents of the tube become homogeneous and blue.

T. H. P.

Fluidity and Conductivity of Some Concentrated Aqueous Salt Solutions below 0°. WILLY HECHLER (*Ann. Physik*, 1904, [iv], 15, 157—173. Compare Lyle and Hosking, *Abstr.*, 1902, ii, 440; Bousfield and Lowry, *Abstr.*, 1903, ii, 52; Kohlrausch, *ibid.*, 403).—Solutions of sodium chloride and iodide, potassium thiocyanate and acetate, calcium chloride, mixed solutions of potassium nitrate and ammonium thiocyanate, and of ammonium nitrate and potassium thiocyanate have been investigated. The convergence points obtained by extrapolation from the conductivity curves are close together in the majority of cases, namely, at -64° to -71° . These, however, do not agree very well with the convergence points obtained by extrapolation from the fluidity curves.

J. C. P.

Comparative Solubility of Gases, &c., in Water and in Aqueous Solutions. GUSTAV GEFFCKEN (*Zeit. physikal. Chem.*, 1904, 49, 257—302).—The solubilities of hydrogen, oxygen, carbon dioxide, and nitrous oxide in water have been determined at 15° and 25° , and are found to have the following values:

| | Hydrogen. | Oxygen. | Carbon dioxide. | Nitrous oxide. |
|--------------------|-----------|---------|-----------------|----------------|
| 15° | 0.01982 | 0.03630 | 1.070 | 0.7784 |
| 25° | 0.01926 | 0.03080 | 0.8255 | 0.5942 |

The solubilities of these gases in solutions of acids, bases, and salts of various concentrations have also been determined. The relative equivalent depression of the solubility has been calculated from the data for each case and is found to be greater at 15° than at 25° . Of nitric, hydrochloric, and sulphuric acids, the first has the least and the last has the greatest influence in lowering the solubility of the above four gases. Indeed, the solubilities of carbon dioxide and nitrous oxide are increased in nitric acid solutions. Both with hydrogen and oxygen, sodium hydroxide lowers the solubility to a greater extent than potassium hydroxide. The order of the salts arranged according to their influence is nearly the same for different gases, and pretty much what has been deduced in other investigations (compare Rothmund, *Abstr.*, 1900, ii, 467; Biltz, *Abstr.*, 1903, ii, 358); here also there are indications of additive relationships. The magnitude of the relative depression of the solubility depends, however, on the nature of the gas, and differs, it is observed, for the otherwise similar gases, carbon dioxide and nitrous oxide; the latter, in fact, behaves in water as an indifferent gas. The power of water to dissolve gases is practically unaffected by the presence of colloids such as ferric hydroxide and arsenic trisulphide.

Electrolytes, when dissolved in water, produce a change in the internal pressure, and this change is very probably connected with the influence they exert on the solubility of gases. To a similar cause

may be referred the deviations from the mass action law exhibited by electrolytes, so far as these are connected with the extent to which the solubility of one electrolyte is influenced by the presence of another. The latter point is illustrated in the paper by a study (1) of the solubility of thallium chloride as increased by ammonium, potassium, sodium, and lithium nitrates, and potassium and sodium chlorates; (2) of the solubility of potassium bromate as increased by sodium nitrate and chloride. The relative influence here of nitrate, chlorate, and chloride is very similar to what it is when the other dissolved substance is a gas or a non-electrolyte. J. C. P.

Determinations of Solubility in Mixtures of Solvents. I. WALTER HERZ and M. KNOCH (*Zeit. anorg. Chem.*, 1904, 41, 315—324).—The authors have determined the solubility of various substances in mixtures of acetone and water.

Acetone, prepared from its sodium hydrogen sulphite compound, remains practically unacted on at the ordinary temperature in contact with potassium permanganate for 24 hours. Determinations of the solubility of potassium permanganate in aqueous acetone of varying concentrations were made at 13°. The solubility rises to a maximum with increase of the amount of acetone and then sinks, the maximum being attained in a mixture containing 3 parts of water to 7 of acetone. The solubility of potassium permanganate in pure acetone is less than in pure water.

The solubility of potassium chloride at 20° sinks as the concentration of acetone increases, and in pure acetone is so slight that it could not be determined. The solubility of sodium chloride is similar except that in this case, with increase of acetone, two layers were formed.

Mercuric chloride appears to form compounds with acetone when the latter is in excess.

The solubility of boric acid at 20° rises to a maximum and then sinks. The solubility of boric acid in pure acetone is slight.

The solubility of succinic acid at 20° rises to a maximum corresponding with a concentration of 3 parts of water to 7 of acetone.

The solubility of barium hydroxide at 25° diminishes very rapidly with increasing concentration of acetone.

With sucrose, two layers separated at the concentration of 55 parts of water to 45 of acetone. The constant, deduced from the values at 25°, was calculated from Bodländer's formula, $W/\sqrt[3]{S}=K$, where W represents the number of grams of water and S the number of grams of dissolved substance in 100 c.c. of solution. A. McK.

Reciprocal Solubility of Oil of Turpentine and Aqueous Alcohol. MAURICE VEZES and MOULINE (*Bull. Soc. chim.*, 1904, [iii], 31, 1043—1049).—Oil of turpentine is miscible with alcohol through a wide range of temperature, but this range becomes greatly restricted when the oil is dissolved in mixtures of alcohol and water. For each mixture of oil, alcohol, and water, separation into two layers occurs at a definite temperature, which varies with the pressure. The "curves of separation" obtained by plotting values of the mass of aqueous

alcohol (z), in unit mass of each of a series of mixtures, as ordinates, and the temperatures of separation, for the same mixtures, as abscissæ, are of the type usually found for binary mixtures (Rothmund, Abstr., 1898, ii, 503), the temperature of separation rising to a maximum and then decreasing as the concentration of alcohol is increased. The curves are not symmetrical, but as a whole lie nearer to the terminal line $z=0$ (turpentine oil) than to $z=1$ (aqueous alcohol) (compare Alexéeff, Abstr., 1886, 847, and Rothmund, *loc. cit.*). Data for alcohols containing respectively 2 and 5 per cent. of water are given in the original. From the nature of these curves, it is shown that (1) the temperature of separation rises as the concentration of water, relative to alcohol, is increased, (2) the solubility of aqueous alcohol in turpentine oil is much less than that of the oil in the aqueous alcohol at the same temperature, and (3) the method of identifying fats by means of their critical solution temperatures (Crismer, Abstr., 1896, ii, 506, and 1903, ii, 10) cannot be generally applicable, since this constant is not practically independent of the concentration as Crismer supposed.

By observing the temperatures of separation for mixtures of oil and alcohol in which the concentration of alcohol in the water-alcohol mixture used varies, a series of isothermal curves of separation was constructed in which the strengths (y) of the alcohols are abscissæ and the masses of aqueous alcohol (z) in the ternary mixtures are ordinates. These curves are similar in form to the foregoing.

T. A. H.

Hydrates in Aqueous Solution. WILHELM BILTZ (*Ber.*, 1904, 37, 3036—3042).—Polemical. A criticism of the theory put forward by Jones (this vol., ii, 386) that the abnormalities in the freezing point of aqueous solutions of electrolytes are due to the formation of hydrates in concentrated solutions, whereas such hydrates do not exist in more dilute solutions.

E. F. A.

Presence of Hydrates in Concentrated Aqueous Solutions of Electrolytes. HARRY C. JONES and FREDERICK H. GETMAN (*Zeit. physikal. Chem.*, 1904, 49, 385—455).—In continuation of previous work (this vol., ii, 386), the authors have determined the freezing points, conductivities, refractive indices, and specific gravities for a large number of concentrated salt solutions. The salts investigated are chiefly the haloids and nitrates of lithium, sodium, potassium, calcium, strontium, barium, magnesium, zinc, cadmium, aluminium, chromium, and iron. The results obtained give further support to the theory previously advanced. From the fact that the most favourable concentration for the formation of hydrates is 0.2—0.3 normal, the authors conclude that the ions also have the power of associating themselves with water molecules.

J. C. P.

Existence of Hydrates in Solutions of Certain Non-electrolytes and the Non-existence of Hydrates in Solutions of Organic Acids. HARRY C. JONES and FREDERICK H. GETMAN (*Amer. Chem. J.*, 1904, 32, 308—338. Compare Abstr., this vol., ii, 386).—The freezing points and sp. gr. of solutions of different concen-

trations of methyl alcohol, ethyl alcohol, *n*-propyl alcohol, acetone, acetamide, carbamide, chloral hydrate, glycerol, dextrose, levulose, mannitol, lactose, and sucrose have been determined, and from the data obtained the extent to which hydrates are formed in each solution has been calculated.

Glycerol is the only one of these non-electrolytes which shows any very marked tendency to form hydrates; the complexity of the hydrate increases regularly from the most dilute to the most concentrated solution investigated. Sucrose and levulose also show considerable hydration, but to a much smaller extent than glycerol. Methyl and ethyl alcohols exhibit a slight power of combining with water in solution. A number of these non-electrolytes, especially propyl alcohol, acetone, carbamide, and lactose, show a tendency to undergo polymerisation in presence of water, and, in such cases, it is impossible to ascertain the extent to which hydration takes place. Acetamide appears neither to form hydrates nor to undergo polymerisation at any dilution. Chloral hydrate, dextrose, and mannitol show very slight hydration.

The freezing points, sp. gr., and conductivity of solutions of acetic, oxalic, succinic, tartaric, and citric acids have been determined. It is found that these acids do not undergo hydration to an appreciable extent. Acetic, oxalic, and succinic acids show a tendency to undergo polymerisation in solution, whilst tartaric and citric acids undergo neither polymerisation nor hydration.

The results of this investigation are tabulated, and the freezing points and conductivity measurements are plotted as curves. E. G.

Existence of Alcoholates in Solutions of Certain Electrolytes in Alcohol. HARRY C. JONES and FREDERICK H. GETMAN (*Amer. Chem. J.*, 1904, 32, 338—342).—A study of the results obtained in some determinations of the elevation of the boiling point of ethyl alcohol produced by certain electrolytes (this vol., ii, 386) has led to the conclusion that, in the cases of sodium bromide and the iodides of cadmium, potassium, ammonium, and sodium, the dissolved salt unites to some extent with the solvent.

In order to obtain further evidence on this point, the molecular rise of boiling point produced by lithium chloride, lithium nitrate, and calcium nitrate has been determined. The results are tabulated and also plotted as curves. It is shown that the molecular elevation in the boiling point of ethyl alcohol, produced by lithium chloride and nitrate, is greater than the value calculated from their dissociation; the same is true for calcium nitrate, but only in dilute solutions. These results are explained as being due to the formation of alcoholates. A certain proportion of the alcohol being thus removed from the sphere of action, there is less acting as solvent, and the rise in the boiling point is consequently greater than would be expected from the amount of dissolved substance present. E. G.

Solid Solutions between Organic Compounds. FELICE GARELLI and FELICE GORNI (*Gazzetta*, 1904, 34, ii, 101—113).—Phenyl salicylate (salol) is a troublesome solvent for cryoscopic measurements,

but if the external bath is kept at about 3° below the freezing point of solution so as to obtain superfusion to the extent of about 2° , and if also care is taken in the stirring, concordant results can be obtained.

From measurements of solutions of naphthalene, azobenzene, bromobenzene, diphenyl, *p*-xylene, benzanilide, acetanilide, and benzoic acid in phenyl salicylate, the molecular freezing point depression for this solvent is found to be about $K=123$.

Phenyl benzoate and salicylresorcinol give abnormally small depressions in phenyl salicylate solutions, whilst salicylquinol raises the freezing point even in very low concentrations. Salicylanilide also forms solid solutions with phenyl salicylate, showing that the groups $\cdot\text{O}\cdot$ and $\cdot\text{NH}\cdot$ in open chains are isomorphogenic.

Measurements of the freezing points of solutions of naphthalene and diphenyl in phenyl benzoate give the value 80 for the molecular freezing point depression of this solvent. In concentrations greater than 1 per cent., acetanilide gives abnormal molecular weights in phenyl benzoate. Benzanilide also gives solid solutions with phenyl benzoate, confirming the isomorphogenic relations of the groups $\cdot\text{O}\cdot$ and $\cdot\text{NH}\cdot$ in open chains. Salol yields abnormally small depressions in phenyl benzoate solution.

Antimony tribromide forms solid solutions with bromoform, showing that Sb, like N, is isomorphogenetic with CH. T. H. P.

Solid Solutions. GIUSEPPE BRUNI and A. TROVANELLI (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 176—184).—The authors have made a series of experiments to ascertain whether oxy-compounds form solid solutions with the corresponding sulphur compounds.

Thioacetic acid gives abnormal molecular weights (99—105 instead of 76) in freezing acetic acid. Thioacetamide yields normal values in acetamide and formamide solutions. Ethyl thiocarbamate gives abnormal values (182—185 instead of 105) and ethyl thioncarbamate normal values in freezing urethane.

Hence, in the aliphatic series, compounds containing the group $:\text{C}\cdot\text{SH}$ (thioacetic acid and ethyl thiocarbamate) give solid solutions with the corresponding derivatives containing the group $:\text{C}\cdot\text{OH}$, while the sulphur compounds, containing the residue $:\text{C}\cdot\text{S}$ (thioacetamide and thioncarbamate), are incapable of crystallising with the corresponding oxygen derivatives.

Thiophenol, however, has the normal molecular weight in freezing phenol, so that the law given above for aliphatic compounds cannot be extended to aromatic derivatives.

p-Chloronitrobenzene exhibits abnormal cryoscopic behaviour in *p*-fluoronitrobenzene, but the abnormality is much less marked when the latter is dissolved in the former. This agrees with previous observations and also with theoretical considerations, which show that, when two isomorphous substances differ markedly in their melting points, the abnormality in molecular weight is the greater when the one with the high melting point is dissolved in the other.

Contrary to the statement of Castoro (*Abstr.*, 1899, ii, 360), acetamide is a good solvent for cryoscopic determinations. T. H. P.

Molecular State of Anhydrous and Hydrated Salts of Metals in Organic Solvents. GIUSEPPE BRUNI and A. MANUELLI (*Zeit. Elektrochem.*, 1904, 10, 601—604).—The depression of the freezing point of urethane and of acetamide produced by copper, nickel, cobalt, and manganese chlorides is determined.

In urethane, the anhydrous salts and water separately give normal freezing point depressions, whereas the two together give small depressions. The results lead to the conclusion that a portion of the water of crystallisation of these salts remains in combination with them when they are dissolved in urethane. When dissolved in acetamide, the anhydrous salts are dissociated to a large extent. When water is added to the solution of the anhydrous salt, it produces the same depression of the freezing point which would be observed with the pure solvent. Except copper chloride, the hydrated salts behave as though the whole of the water was split off. Copper chloride appears to retain $\frac{1}{2}\text{H}_2\text{O}$. The decomposition may be due to the high temperature (82°) or to the combination of the salts with acetamide itself. T. E.

Order of Magnitude of the Time of Formation of Complex Molecules, Equilibrium Constants, and Atomic Dimensions. GUIDO BODLÄNDER (*Zeit. Elektrochem.*, 1904, 10, 604—607).—Referring to Haber's paper on this subject (this vol., ii, 607), the author suggests that the active mass of a dissolved substance is not necessarily proportional to its concentration, and that the extremely small active masses calculated from *E.M.F.*s may correspond with much larger concentrations. There are no grounds for doubting the reality of the small active masses calculated; in some cases (for example, a solution of silver chloride in an alkali chloride) they may be shown analytically to exist. The difficulty which Haber sees in the rapid chemical reactions which occur in solutions containing complex ions may be avoided by supposing that the complex ions react directly and do not first dissociate into simple metallic ions. For example, the precipitation of silver sulphide from a solution of potassium silver cyanide may take place as follows: $2\text{Ag}(\text{CN})_3'' + \text{S}'' \rightleftharpoons \text{Ag}_2(\text{CN})_6\text{S}'''''$ and $\text{Ag}_2(\text{CN})_6\text{S}''''' = \text{Ag}_2\text{S} + 6\text{CN}'$. This would be analogous to the decomposition of silver potassium thiosulphate. The electrolytic deposition of silver from such a solution might occur by the $\text{Ag}(\text{CN})_3''$ ion first taking up a negative charge at the cathode, forming the unstable ion $\text{Ag}(\text{CN})_3'''$, which would then decompose into Ag and $3(\text{CN})'$.

RICHARD ABEGB (*ibid.*, 607—609) considers that the fact that an electrode is very much more completely and rapidly depolarised by a solution containing a complex salt of a metal than by a dilute solution of a salt of the same metal containing the same number of metallic ions proves that the metallic ions are formed from the complex ions with great velocity. The observations of Brereton Baker on the effects of minute quantities of water on chemical reactions are cited as showing that very small quantities of ions are capable of producing rapid reactions. The author also takes the view that many organic reactions are due to quantities of ions which are much smaller than even the smallest calculated in solutions of inorganic substances.

H. DANNEEL (*ibid.*, 609—610) holds that the shortest time in which a chemical change can take place is not necessarily so long as that calculated by Haber. If the reacting molecules are in contact, it may be infinitely small. T. E.

Diminution in the Velocity of Crystallisation caused by Foreign Substances. MAURICE PADOA and D. GALEATI (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 107—111. Compare Dreyer, *Abstr.*, this vol., ii, 611).—The authors criticise the calculations and results of von Pickardt (*Abstr.*, 1903, ii, 66). They have measured the velocities of crystallisation of α -naphthylamine, diphenylamine, benzil, and benzophenone, both in the pure state and when mixed with varying proportions of various substances of widely-differing molecular weights. The maximum velocity was taken as the observed value, and not an extrapolated value as was done by von Pickardt. The results with benzophenone correspond with those obtained by von Pickardt and do not obey the laws laid down by this author, to the effect that molecular quantities of dissolved substances lower the velocity of crystallisation of the solvent to the same extent and that this lowering is proportional to the square root of the concentration of the solute. Cryoscopic measurements show that the substances dissolved in benzophenone possess normal molecular weights. Liquids have a greater influence on the velocity of crystallisation than solids.

The phenomena of crystallisation are very complex and probably depend on the internal friction of the melted mass. T. H. P.

Proof of the Nature of Liquid Crystals by Aid of Electric Kataphoresis. GEORG BREDIG and G. VON SCHUKOWSKY (*Ber.*, 1904, 37, 3419—3425. Compare Tammann, *Abstr.*, 1902, ii, 445; Rotarski, *Abstr.*, 1903, i, 869; Schenk and Eichwald, this vol., i, 118; de Kock, this vol., ii, 548).—If a current of electricity, at a potential varying from 72 to 20,000 volts, is passed through a suspension of shellac in water, the shellac particles immediately gather at the anode and in 5 minutes the separation is distinct to the unaided eye. Under the microscope, with an *E.M.F.* of 70 volts, the separation can be observed almost instantaneously.

If the so-called liquid crystals are really emulsions, separation should take place in this manner. With the liquid crystals of *p*-azoxyanisole, anisaldazine, the condensation product of benzaldehyde and benzidine, and the condensation product of *p*-tolualdehyde and benzidine, no such separation took place when a current, at potentials varying from 72 to 48,000 volts, was passed through them for 10 minutes to 3 hours. With cholesterol propionate, in three experiments at an *E.M.F.* of 72 volts, the current passing for 60—100 minutes, the liquid at the cathode appeared to become clearer, but no change took place on reversing the current. G. Y.

New Points in the Theory of Colloids. EDUARD JORDIS (*Zeit. Elektrochem.*, 1904, 10, 509—518).—With the exception of silver, all inorganic colloids are formed from elements of valency higher than unity. The salts of all these elements are hydrolysed in aqueous solution. The formation of the colloid is regarded as the final result

of the continued hydrolysis. The pure hydroxides never form hydrosols; when the content of acid or alkali is reduced below a certain point, the colloid invariably separates as a hydrogel. Even in Bredig's metallic colloid solutions, the author thinks that a sufficient quantity of alkali or other impurity would be present to form a hydrosol. The small quantity of acid or alkali required to form a hydrosol is supposed to be combined with the colloid in the form of an ion, so that the colloid has an electric charge; this charge changes its surface tension: as long as the surface tension is the same as that of the liquid, the colloid remains in the hydrosol form; having the same surface tension as the liquid, it is indistinguishable from it, but is nevertheless merely a suspended solid. The formation of the hydrogel is due to the charge changing, and with it the surface tension.

T. E.

Stability of the Equilibrium of Multivariant Systems. PAUL SAUREL (*J. Physical Chem.*, 1904, 8, 488—490).—An extension of the theorems deduced concerning the stability of a bivalent system (this vol., ii, 643). The theorems are obtained by replacing "trivariant" and "bivalent" for "bivalent" and "univalent" in the previous paper. The theorems may be further extended to any multivariant systems.

L. M. J.

Indifferent Points. PAUL SAUREL (*J. Physical Chem.*, 1904, 8, 491—492).—A multivariant system is at an indifferent point when it admits of a series of equilibrium states during which temperature, pressure, and concentrations remain constant while the masses of the phases change. The temperature of the indifferent point is, in general, a maximum or a minimum of the temperatures at which the system is in equilibrium under the given pressure, and the pressure similarly a maximum or a minimum for the given temperature. If for a reversible change the changes of entropy and volume have the same sign, the maximum pressure is associated with a minimum temperature and a minimum pressure with a maximum temperature. If, however, the changes of entropy and volume have different signs, then maxima (or minima) of pressure and temperature are associated.

L. M. J.

Equilibrium between Silver Salts. RICHARD LUCAS (*Zeit. anorg. Chem.*, 1904, 41, 193—215).—When potassium chloride is agitated with silver cyanide, the complex potassium silver cyanide is formed and silver chloride separates. This reaction proceeds almost instantaneously. When potassium silver cyanide is agitated with silver chloride, potassium chloride is formed and silver cyanide separates. In the reaction $\text{Ag} \cdot \text{Ag}(\text{CN})_2 + \text{KCl} \rightleftharpoons \text{K} \cdot \text{Ag}(\text{CN})_2 + \text{AgCl}$, silver chloride and silver cyanide separate as solid phases; their active masses are accordingly constant and the following relationships exist: $[\text{Ag}^*][\text{Ag}(\text{CN})_2] = K_1$ and $[\text{Ag}^*][\text{Cl}'] = K_2$, where K_1 and K_2 represent the solubility products of the solid phases. Equilibrium is established when $[\text{Ag}(\text{CN})_2]/[\text{Cl}'] = K_1/K_2 = \text{constant}, K$. The latter value was found by experiment to be 0.0260 at 25°; it remains the same whether

equilibrium is established between silver cyanide and potassium chloride or between potassium silver cyanide and silver chloride. When the solubility product of one of the sparingly soluble salts is known, the value for the other is readily determined. Thus the solubility product of silver chloride at 25° is $(1.41 \times 10^{-5})^2$, whence that for silver cyanide is 0.0260 (1.41×10^{-5})², whilst the solubility is 2.27×10^{-6} . When the solubility of silver cyanide was determined by using silver bromide instead of silver chloride, the value 2.19×10^{-6} was obtained, a value which was also obtained when silver thiocyanate was used. The mean value was accordingly 2.2×10^{-6} , a value at variance with that deduced by Böttger from determinations of electrical conductivity. The interaction between potassium iodide and silver cyanide is very complete.

A different value for the solubility of silver cyanide, namely, 0.485×10^{-6} , is, however, obtained from experiments on the solubility of silver cyanide in ammonia (compare Bodländer and Fittig, *Abstr.*, 1902, ii, 248). The complex ion $\text{Ag}(\text{NH}_3)_2^+$ is present, whilst the complex salt formed is only slightly dissociated, the degree of dissociation increasing only slightly with increasing dilution. The dissolved salt has the formula $\text{AgCN} \cdot \text{NH}_3$, and it is dissociated according to the equation $2\text{AgCN} \cdot \text{NH}_3 = \text{Ag}(\text{NH}_3)_2^+ + \text{Ag}(\text{CN})_2^-$. The influence on the solubility of silver cyanide in ammonia exerted by the addition of other silver salts was also examined.

Owing to the slight solubility of silver cyanide in ammonia, the lowering of the freezing point was small.

Measurements of the electrical conductivity of silver cyanide in ammonia showed that the specific conductivity varied only slightly from that of ammonia. Interaction between silver iodide and potassium cyanide is expressed by $\text{AgI} + 2\text{KCN} = \text{KAg}(\text{CN})_2 + \text{KI}$. The action is complete when the number of silver ions liberated from silver iodide is as great as the number from the decomposition of the complex ions. The ratio $[\text{CN}]/[\text{Ag}(\text{CN})_2]$ is 2.83×10^{-3} .

Silver sulphide is less soluble than silver iodide both in water and in aqueous potassium cyanide. The solubility product of silver sulphide is $[\text{Ag}^+]^2[\text{S}^{2-}] = 17.9 \times 10^{-49}$. In order to determine the solubility of silver sulphide in potassium cyanide, the former was agitated at 25° with solutions of potassium cyanide of varying strengths. In solutions stronger than $N/0.05$, the complex silver salt $\text{K}_2\text{Ag}(\text{CN})_3$ is formed, thus: $\text{Ag}_2\text{S} + 6\text{KCN} + \text{H}_2\text{O} = 2\text{K}_2\text{Ag}(\text{CN})_3 + \text{KSH} + \text{KOH}$. The solubility of silver sulphide in potassium cyanide is 1.66×10^{-17} . From the relationship deduced by Bodländer between solubility and heat of formation, the electric potential of sulphur towards hydrogen is determined to be -0.59 volt.

A. McK.

Theoretical Consideration of Reactions which take place in Two or More Successive Stages. COENRAAD L. JUNGUS (*Zeit. physikal. Chem.*, 1904, 49, 368—375).—In reference to Smits and Wolff's experiments on the velocity of transformation of carbon monoxide (*Abstr.*, 1903, ii, 276, 638), the author shows that chemical processes which are of the first order, but really take place in two or

more stages, may be reversible. In other words, there may be incomplete reactions, the course of which does not harmonise with the number of molecules occurring in the chemical equation. In such a case, the usual formula, $dx/dt = k.C_1^m.C_2^n \dots - k'.C_1'^m.C_2'^n \dots$ cannot be applied, and the experiments may not point to any definite order of reaction. On the other hand, the chemical equation may be taken as a basis for the determination of the equilibrium constant.

J. C. P.

Application of the Phase Rule to Mixtures of Iron and Carbon. H. W. BAKHUIS ROOZEBOOM (*Zeit. Elektrochem.*, 1904, 10, 489—491).—The author reproduces the diagram given previously (Abstr., 1900, ii, 728), with a few small alterations in the positions of the lines due to more recent experiments.

T. E.

Reaction Velocity and Free Energy. MAX BODENSTEIN (*Zeit. physikal. Chem.*, 1904, 49, 61—69).—One of the chief problems of chemical kinetics is the determination of reaction velocity (V) in absolute units, and the discovery of the relationship between this and the other factors concerned, namely, the driving force (F) of the reaction and the chemical resistance (R). It is probable that these are connected by an expression analogous to Ohm's law, and that $V = F/R$, but R especially, made up as it is of the most diverse factors, is as yet far from susceptible of quantitative determination. As a beginning, however, to the study of these relationships, the author proposes a complete investigation of the velocities and equilibria characteristic of the combination of hydrogen with the halogens, cases which are unaffected by catalysts, and in which the course of reaction is in harmony with Guldberg and Waage's fundamental views of the relationship of velocity and equilibrium. Reichenbach has accordingly made a preliminary study of the rate of union of hydrogen and bromine with promising results. By a method similar to that used in another investigation (Bodenstein, Abstr., 1893, ii, 369; 1894, ii, 12; 1897, ii, 252), the course of change can be conveniently followed between 228° and 328°, within which range the reaction is practically non-reversible. An experiment at 650—750° showed that hydrogen bromide is dissociated under these conditions to the extent of 0.3—0.9 per cent.

J. C. P.

Dissociation of Hydrogen Bromide and Hydrogen Chloride. MAX BODENSTEIN and ARTHUR GEIGER (*Zeit. physikal. Chem.*, 1904, 49, 70—81. Compare Bodenstein, preceding abstract).—The extent of dissociation of hydrogen bromide and hydrogen chloride cannot be accurately determined by the method used in the case of hydrogen iodide (Bodenstein, 1893, ii, 369; 1894, ii, 12; 1897, ii, 252) because of the high velocity of the reactions involved. The relationship, however, between chemical equilibrium and electromotive force (see Knüpfner, Abstr., 1898, ii, 420; Dolezalek, *ibid.*, 421) furnishes the required result, which is, in the first place, the value of K , the equilibrium constant. The data necessary in the case of hydrogen chloride are obtainable from Dolezalek's paper (*loc. cit.*), and

those necessary in the case of hydrogen bromide are recorded in the present paper. It follows from these that at 30° the percentage dissociation of hydrogen bromide is 6×10^{-8} , whilst that of hydrogen chloride is 6.6×10^{-15} . The degrees of dissociation at higher temperatures may be deduced from the equation $d(\log K)/dT = -q/RT^2$, for q is known in each case, and its variation with temperature can be calculated. In this way the following values have been obtained for the percentage dissociation at high temperatures:

| | Hydrogen chloride. | Hydrogen bromide. |
|---------------|---------------------|-------------------|
| 600° abs..... | 15×10^{-7} | 0.0035 |
| 1000 „ | 0.002 | 0.18 |
| 2000 „ | 0.8 | 6.0 |

J. C. P.

Oxidation of the Iodine Ion to Hypoiodite as an Intermediate Stage in Several Reactions. JOHANNES BRODE (*Zeit. physikal. Chem.*, 1904, 49, 208—216. Compare Noyes and Scott, *Abstr.*, 1896, ii, 158; Brode, *Abstr.*, 1901, ii, 443; Brédig and Walton, *Abstr.*, 1903, ii, 282).—The following reactions are compared: I, $2\text{H}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{O}_2$, catalytically accelerated by iodine ions in neutral solution; II, $\text{H}_2\text{O}_2 + 2\text{HI} = 2\text{H}_2\text{O} + \text{I}_2$, in acid solution; III, $\text{H}_2\text{O}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 + 2\text{H}^+ = 2\text{H}_2\text{O} + \text{Na}_2\text{S}_4\text{O}_6 + 2\text{Na}^+$, catalytically accelerated by iodine ions in dilute acid solution. It is shown that in each case the course of change is governed by the equation $dx/dt = kc_1c_2$, where c_1 and c_2 are the concentrations of peroxide and iodine ions respectively. The velocity constants thus obtained for reactions II and III are equal, and half the value of the constant for reaction I. It is therefore supposed that in all three cases the velocity really measured is that of the intermediate reaction, $\text{H}_2\text{O}_2 + \text{I}' = \text{H}_2\text{O}_2 + \text{OI}'$, and that the double velocity in reaction I is due to a very rapid interaction of the hypoiodite with another peroxide molecule, thus: $\text{OI}' + \text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{O}_2 + \text{I}'$.

The author doubts whether any reaction of the first order is known that takes place at a measurable rate without a catalyst. Where a catalyst is necessary, there may be an intermediate reaction, as in the case considered above, and the reaction really studied is then one of the second order. The author, in fact, considers that in all reactions the governing formula is $dx/dt = kc_1c_2$ (or kc^2), and that any deviation from the course required by this formula is due to the superposition of several velocities.

J. C. P.

Rate of the Reaction between Iodic and Hydriodic Acids. SAUL DUSHMAN (*J. Physical Chem.*, 1904, 8, 453—482).—The rate of the reaction in acetic acid solutions was determined. It was found that the rate was proportional to the second power of the concentration of the hydrogen ion, to the first power of the concentration of the iodate ion, and approximately to the second power of the concentration of the iodine ion. With iodine in excess, that is, with the tri-iodine ion present in excess, the rate was proportional to the square of the concentration of the hydrogen ion and to the first power of the

concentration of both the iodine and tri-iodine ions. These results suggest equations in which the left-hand sides are respectively $2\bar{I} + 2\bar{H} + \bar{IO}_3 =$ and $\bar{I} + \bar{I}_3 + 2\bar{H} + \bar{IO}_3 =$. The right-hand side of the first is probably $2HOI + \bar{IO}$, but that of the second equation is doubtful. The authors offer the suggestion $HI + HI_3 + \bar{IO}_3 = HOI + HOI_2 + \bar{IO}$, in which the hypothetical HOI_2 decomposes into I_2 and HOI .

L. M. J.

Enzyme Action. I. H. P. BARENDRECHT (*Zeit. physikal. Chem.*, 1904, 49, 456—482).—Fuller details are given of work already reported (this vol., ii, 551). The equation governing the inversion of sucrose by invertase is $-dx/dt = mx/[x + n(a - x)]$, where a is the initial number of grams of sucrose in 100 c.c. of water, m is the quantity of invert sugar produced in the first minute, x is the unchanged sucrose at time t , and n is the absorptive power of invert sugar for the enzyme radiation relatively to that of sucrose. The data recorded by Brown (*Trans.*, 1902, 81, 377) are in harmony with this equation, and also with the modified equation $-dx/dt = m.x/[x + n(a - x) + 0.5b]$, which provides for the case where b grams of dextrose or lævulose are initially present.

The synthetical action of enzyme radiation is further discussed, and formulæ are given for the cases in which the products of inversion undergo a secondary change before reversion can take place. The author's results are in harmony with Simon's views (*Abstr.*, 1901, i, 256) rather than with those of Armstrong (*Trans.*, 1903, 83, 1305) and Lowry (*Trans.*, 1903, 83, 1314).

J. C. P.

Heterogeneous Catalytic Reactions. II. Autocatalysis in Heterogeneous Systems. MAX BODENSTEIN (*Zeit. physikal. Chem.*, 1904, 49, 41—60. Compare this vol., ii, 245).—Besides showing, as previously reported (this vol., ii, 413), that the decomposition of antimony hydride is a case of autocatalysis, and that the corresponding equation, $dx/dt = k(m + x)(a - x)$, represents the actual course of the reaction as determined by Stock and Guttman (this vol., ii, 246), the author deals with other cases of autocatalysis in heterogeneous systems. Thus Cohen's observations on the decomposition of arsenic trihydride (*Abstr.*, 1896, ii, 593; 1898, ii, 328) and the author's observations on the decomposition of hydrogen selenide (*Abstr.*, 1899, ii, 639) may be quantitatively reproduced with the aid of the above equation. The decomposition of sodium thiosulphate by acids is an analogous case, for the sulphur formed in the reaction behaves as a catalyst, and it is found that Foussereau's numbers (*Ann. chim. Phys.*, 1888, [vi], 15, 533) are in fair agreement with the demands of the above equation.

J. C. P.

Catalysis of Ethyl Acetate by Nitric Acid in Presence of Alkali Nitrates. HARALD LUNDÉN (*Zeit. physikal. Chem.*, 1904, 49, 189—198. Compare Euler, *Abstr.*, 1900, ii, 269).—For every 0.1

equivalent of potassium or sodium nitrate, the velocity of catalysis of ethyl acetate by nitric acid increases by 2.3 per cent.; this effect is half as great as the corresponding influence of chlorides on hydrochloric acid. The neutral salt action ("Neutralsalzwirkung") of the nitric acid itself is also about half that of hydrochloric acid.

The influence of the various ions on the velocity of catalysis is formulated thus:

$$K_{\text{HCl}} = A \cdot m_{\text{H}}(1 + a \cdot m_{\text{H}} + b \cdot m_{\text{Na}} + c \cdot m_{\text{Cl}})$$

$$K_{\text{HNO}_3} = A \cdot m_{\text{H}}(1 + a \cdot m_{\text{H}} + b \cdot m_{\text{Na}} + d \cdot m_{\text{NO}_3}),$$

where m is ionic concentration and A, a, b, c, d are constants. From the author's experiments, the values of the constants are: $A = 304$ (± 5), $a + c = 0.34$ (± 0.10), $b + c = 0.58$ (± 0.02), $a + d = 0.18$ (± 0.02), $b + d = 0.42$ (± 0.06). J. C. P.

Disintegration of Elements. HUGO KAUFFMANN (*Zeit. angew. Chem.*, 1904, 17, 1393—1397).—A theoretical paper. A. McK.

Supposed Change in Weight during Chemical Reactions. ANTONINO LO SURDO (*Nuovo Cimento*, 1904, [v], 8, 45—67).—The author describes the methods employed by him to determine whether any change of weight occurs in the reaction taking place between iron and a basic solution of copper sulphate. The variations obtained are so nearly equal to the errors of experiment that it is concluded that no alteration in weight occurs in this reaction. T. H. P.

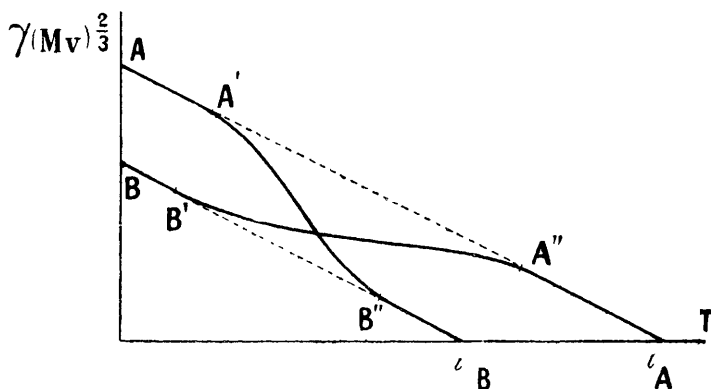
Atomic Weight of Radium and Relationships between the Atomic Weights of the Elements and their Spectra. W. MARSHALL WATTS (*Phil. Mag.*, 1904, 8, 279—284).—The author calculates the atomic weight of radium by the law of Runge and Precht from the various pairs of the four elements, magnesium, calcium, strontium, and barium. The values vary between 222.7 and 263.6. The author considers the method of calculation gives results considerably too high. Calculations of the atomic weights of series of elements by the same law show that lithium and sodium give values approximately correct if considered in a series with copper, silver, and gold, but not when considered in series with potassium, rubidium, and caesium. Similarly, magnesium fits in better with calcium and strontium than with zinc and cadmium. L. M. J.

Chemical Valency. JEAN BILLITZER (*Monatsh.*, 1904, 25, 745—773).—The author considers that the valency of an element varies with the temperature; thus at the ordinary temperature carbon is quadrivalent, and therefore acetylene is an unsaturated compound, but at high temperatures, as that of the electric arc, carbon is bivalent and acetylene is formed as a saturated substance. Where a reaction is accompanied by a change in volume, the valency of an element may be effected by changes of pressure. At 3000° under a pressure of 0.001 atmosphere, 94 per cent. of carbon dioxide decomposes into carbon monoxide and water, whereas under 100 atmospheres pressure only 10 per cent. of carbon dioxide is decomposed. In both cases the carbon partly becomes bivalent, the higher pressure favouring quadri-

valency. The valencies of the elements in a group of the periodic system vary inversely with the vapour tension. G. Y.

Passivity of Metals. OTTO SACKUR (*Chem. Zeit.*, 1904, 28, 954—956).—An historical survey dealing with the passivity of metals. A. McK.

Recognition of Tautomerism in Liquids. RUDOLF SCHENCK and E. ELLENBERGER (*Ber.*, 1904, 37, 3443—3453).—The authors discuss tautomerism in liquids which do not undergo association. The molecular surface energy $\gamma(Mv)^{2/3}$ (Ramsay and Shields, *Trans.*, 1893, 63, 1089; *Abstr.*, 1894, ii, 179) is plotted against temperature. The curve in the case of a pure liquid is a straight line. For the two distinct modifications A and B of a tautomeric liquid, two parallel straight lines would be obtained, but for a mixture of the two which changes in composition with the temperature a curve would be obtained, for example, in Fig. AA' or BB'. Similarly if the temperature-coefficient K is calculated from the equation $\gamma(Mv)^{2/3} = K(2 - t - d)$.



For a normal liquid, the value is 2.12 Erg., but for one exhibiting tautomerism the value first approximates to the normal, then reaches a maximum, and then again approximates to the normal value, or, starting near the normal value, it reaches a minimum and again approximates to the normal value.

The latter case can be distinguished from variations due to association by determining the values at sufficiently low temperatures. In cases of association, the coefficient continues to decrease with the temperature, but with tautomerism a minimum is reached and then the coefficient again approaches the normal value. Dibenzoylacetone in a fused state, acetylacetone, and ethyl acetoacetate have been examined and the results confirm those obtained by previous investigators. For example, ethyl acetoacetate consists of one modification only (the ketonic) at all temperatures up to about 140°. J. J. S.

A Modified Kipp Apparatus. JOSEF LOCZKA (*Chem. Zeit.*, 1904, 28, 729, 730).—The apparatus consists of a 3-necked Woulf's

flask, above which is placed an acid container, the tapped stem of the latter passing down through the middle neck nearly to the bottom of the flask. The lower part of this stem is perforated and is surrounded by a glass tube. After placing a layer of pumice-stone in the flask, sufficient ferrous sulphide, marble, &c., according to the kind of gas which it is desired to produce, is added, and the acid allowed to run down from the upper vessel. The gas evolved is drawn by means of a tapped delivery tube leading from one of the necks of the flask. Any excess of acid running into the flask is caused to return to the acid container by a tube passing through the third neck of the flask and reaching from the bottom of the latter to the upper part of the acid vessel. All the tubes are of glass and the joints are ground in.

W. P. S.

New Form of Wash-bottle and Safety Bunsen Burner.

RUDOLF L. STEINLEN (*Chem. Zeit.*, 1904, 28, 753).—The tube forming the mouth-piece of the wash-bottle reaches to the bottom of the latter and at its lower end is provided with a valve, which consists of a short dumb-bell-shaped piece of glass rod placed between two constrictions in the tube. With the upper constriction the rod forms an air-tight joint, but not with the lower. A similar valve, working in the opposite direction, is placed at the bottom of the delivery tube of the wash-bottle. The cork of the bottle has also passing through it a third short tube provided with a stopper-valve at its upper end, which is worked by the finger and serves as a safety-valve to the wash-bottle.

The safety Bunsen burner described is intended for use under water and air-baths. The flame is surrounded by a large inverted cone of fine copper gauze, the apex of which is clamped to the tube of the burner. The flat base of the cone also serves as a support for evaporating basins, &c.

W. P. S.

A New Rapid Filter. G. GIEMSA (*Chem. Zeit.*, 1904, 28, 752—753).—A number of glass rods are placed in an ordinary funnel. The upper ends of the rods are bent over to hook on the rim of the funnel, whilst the lower ends just reach to the junction of the conical part of the funnel with the stem. The apparatus filters thick solutions more quickly than do the ordinary ribbed funnels.

W. P. S.

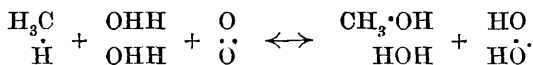
A New Incinerator. PH. SCHNEIDER (*Chem. Zeit.*, 1904, 28, 781).—The author modifies an ordinary combustion oven, so that it can be used for incinerations or for volatilising ammonium salts.

W. A. D.

Inorganic Chemistry.

Dissociation Points of Some Chlorides. PETER FIREMAN and EDWARD G. PORTNER (*J. Physical Chem.*, 1904, 8, 500—504).—If potassium iodide is brought close to the fumes given off by antimony pentachloride, a brown precipitate of iodine forms on the surface of the iodide. Other dissociable chlorides act similarly either cold or when heated, and the authors have endeavoured, by ascertaining the temperatures at which potassium iodide starch papers were coloured, to determine the dissociation temperature of these chlorides. The results obtained are as follows: phosphorus pentachloride, 157—158°; ferric chloride (anhydrous), 122—123°; cupric chloride (anhydrous), 344°; chromic chloride (anhydrous), 355°. L. M. J.

Retardation of Combustion by Oxygen. HENRY E. ARMSTRONG (*Proc. Roy. Soc.*, 1904, 74, 86—89).—A theoretical paper. The initial stage of the combustion of a hydrocarbon is its hydroxylation; a stage is soon reached when “thermoschisms” begin, thus, dihydroxymethane breaks up as soon as it is formed into water and formic aldehyde, which is then converted into hydrogen and carbon monoxide. The more complex hydrocarbons are resolved into simpler “thermoschisms” prior to oxidation. The combustion of methane is represented as follows:



Carbon dioxide is a later product of change than the monoxide. The influence of oxygen in retarding combustion is noteworthy in the case of electrolytic gas. A. McK.

Union of Hydrogen with Sulphur, Selenium, and Tellurium. FRANCIS JONES (*Mem. Manchester Phil. Soc.*, 1904, 48, xvi, 1—5).—Boiling sulphur was found to combine with hydrogen, dried with sulphuric acid and phosphoric oxide. On heating in a current of carbon dioxide similarly dried until no formation of hydrogen sulphide could be noticed and then introducing moisture into the gas stream, considerable formation of hydrogen sulphide ensued.

Sulphur and hydrogen were also found to unite completely on heating together in a sealed tube in a bath of boiling sulphur.

Sulphur, selenium, and tellurium were all readily combined with hydrogen when heated in the closed end of a tube filled with that gas and dipping at its open end into sodium hydroxide solution.

G. D. L.

Condition of Hydrogen Sulphide in Mineral Wells. FRIEDRICH AUERBACH (*Zeit. physikal. Chem.*, 1904, 49, 217—223).—The author has determined the dissociation constant of hydrogen

sulphide at 18° , and finds the value 0.91×10^{-7} , which is intermediate between the values given by Walker and Cormack (*Trans.*, 1900, 77, 5) and Paul (*Chem. Zeit.*, 1899, 23, 535). With the aid of this number and the corresponding one for carbonic acid (Walker and Cormack, *loc. cit.*), the author calculates the proportion of free and combined carbonic acid and hydrogen sulphide in several mineral waters of which analyses are available. A similar calculation may be made in the case where carbonic and boric acids are present together, and it appears that when the quantity of carbon dioxide is considerable the boric acid is practically all present in the free state (compare Grünhut, this vol., ii, 615). Under similar conditions, silicic and titanitic acids are practically free and undissociated, and there are practically no CO_3 ions. J. C. P.

Catalytic Preparation of Sulphur Trioxide. GEORG LUNGE and K. REINHARDT (*Zeit. angew. Chem.*, 1904, 17, 1041—1051. Compare *Abstr.*, 1903, ii, 70).—The catalytic formation of sulphur trioxide from dry sulphur dioxide and atmospheric oxygen by means of ferric oxide is perceptible at a temperature slightly exceeding 400° , and attains its maximum of about 70 per cent. at 625° , above which the action decreases in intensity. It is immaterial whether the gases are dried by sulphuric acid and then by phosphoric oxide, or by sulphuric acid alone. Mixtures of arsenious oxide and ferric oxide have much the same influence on the catalytic formation of sulphur trioxide as has ferric oxide itself. Interaction between sulphur dioxide and oxygen proceeds to the extent of 70 per cent. at 625° when ferric arsenate is used as the catalyser. Ferric arsenite is not so suitable. Arsenic oxide is a very suitable catalyser, the maximum being attained at about 681° . The addition of small amounts of copper sulphate or of copper oxide to ferric oxide has no influence on the catalysis, whilst larger amounts of copper oxide decrease the rate of action. Copper oxide itself has a very slight catalytic action. The action of Jena glass or Berlin porcelain is very slight and cannot be detected below 700° . Silica, on the other hand, in the form either of rock-crystal or of amorphous quartz-glass, has an appreciable influence. A. McK.

Phenomena observed during the Electrolysis of Concentrated Sulphuric Acid. B. G. COBB (*Chem. News*, 1904, 90, 26—27).

Behaviour of Sulphites towards Wood and Tanning Materials HANS BUCHERER (*Zeit. angew. Chem.*, 1904, 17, 1068—1073).—In the recovery of sulphur dioxide from the waste liquors from the manufacture of cellulose, calcium monosulphite is formed by the addition, first, of milk of lime, and finally of chalk. By this method, the solution is kept acid, and the amount of sulphur dioxide recovered is small, since the greater part of it remains combined with organic substances, possibly in the form of esters of sulphurous acid, which are much more stable in acid than in alkaline solutions.

It is not possible to estimate directly the amount of sulphur

dioxide in the liquors by means of iodine, since aldehydic substances are present. When the liquors are distilled with hydrochloric acid and the sulphur dioxide thus expelled passed into an alkali hydroxide, which is then titrated with iodine, the results vary with the time the distillation has been conducted, since the organic compounds of sulphur dioxide are gradually decomposed by the mineral acid with the evolution of sulphur dioxide. The author has studied the behaviour of the sulphite waste liquors towards dilute sulphuric and hydrochloric acids, calcium carbonate, calcium hydroxide, and dilute sodium hydroxide.

The amount of milk of lime necessary for the formation of calcium monosulphite from the liquor is determined by distilling an aliquot portion of the latter with hydrochloric acid until no more sulphur dioxide passes over, and then adding milk of lime to the residue until the reaction is distinctly alkaline towards phenolphthalein. Sufficient milk of lime is added to the liquors to ensure a distinctly alkaline reaction at the completion of the action, in order that all the organic compounds of sulphur dioxide present may be decomposed.

The behaviour of sulphites towards tanning materials has also been examined. Sulphites can act as sulphonating agents without any reduction being caused with the substance acted on. When the product, obtained by the action of sulphites on resorcinol, is treated with alkali, a substance is obtained which is insoluble in ether and is regarded as a sulphonic acid. Resorcinol (1 mol.) unites with sodium hydrogen sulphite (3 mols.) to form a product in which sulphur dioxide cannot be detected by means of iodine. Trihydroxybenzene derivatives and tanning materials do not, however, form esters of sulphurous acid in the manner resorcinol does. A. McK.

Hyposulphites. HANS BUCHERER and ARTHUR SCHWALBE (*Zeit. angew. Chem.*, 1904, 17, 1447—1451).—According to Schützenberger, sodium hyposulphite has the formula NaHSO_2 , and, according to Bernthsen, NaSO_2 or $\text{Na}_2\text{S}_2\text{O}_4$. The grounds on which those formulæ are assigned are discussed.

According to the author, sodium hyposulphite, obtained by salting out from an aqueous solution, contains at least 1 mol. of water of constitution, and the formula $\text{O} < \begin{smallmatrix} \text{SHO} \cdot \text{ONa} \\ \text{SHO} \cdot \text{ONa} \end{smallmatrix}$ is assigned to it.

It has two hydrogen atoms replaceable by metals; it is neutral towards litmus. With formaldehyde, it forms an additive compound, which condenses with amines. A. McK.

Oxidation of Nitrogen. Comparative Yields by Division of the Current. FRANZ VON LEPEL (*Ber.*, 1904, 37, 3470—3474).—When a current of 6 amperes and 14 volts is sent through 2 parallel discharge tubes by means of a Wagner Commutator, practically the same amount of nitric acid is obtained in each as would be produced by passing the same current through a single tube. Further division of the current is not economical. Comparative experiments made with a Wehnelt and a Wagner Commutator with stationary electrodes indicate that the Wagner is the more economical.

Experiments have also been made by dividing the current in a single vessel by means of a forked rotating anode on a flat cathode.

The results indicate that the length of spark, the rate at which air enters, the nature of the electrodes and of the cathode liquid, and also the velocity of rotation of the anode all affect the yield. When the rotation is rapid, a slower current of air can be used; the best yields are obtained by rotating the anode with a moderate velocity and sending in a moderate supply of air. J. J. S.

The Constitution of the Ammonium Compounds. JOHN C. CAIN (*Mem. Manchester Phil. Soc.*, 1904, 48, xiv, 1—11).—The author suggests that the ammonium compounds are formed from ammonia owing to the assumption on the part of a halogen or oxygen (or sulphur) atom of higher valency. Thus ammonium hydroxide, ammonium chloride, and phenyldiazonium chloride are respectively formulated: $\text{H}_3\text{N}:\text{OH}_2$, $\text{H}_3\text{N}:\text{ClH}$, $\text{Ph}\cdot\text{N}\begin{smallmatrix} \text{Cl} \\ | \\ \text{N} \end{smallmatrix}$. G. D. L.

Density of Nitrous Oxide. LORD RAYLEIGH (*Proc. Roy. Soc.*, 1904, 74, 181—183. Compare Abstr., 1898, ii, 290).—In view of the higher value (1.5301) obtained by Leduc for the density of nitrous oxide, the author has carried out a fresh determination, purifying the gas with the aid of liquid air. The value now found is 1.5297.

J. C. P.

Hydrates of Nitric Acid. FRIEDRICH W. KÜSTER and ROBERT KREMANN (*Zeit. anorg. Chem.*, 1904, 41, 1—42).—A reply to Erdmann (Abstr., 1903, ii, 73. Compare Erdmann, this vol., ii, 26, and Küster, this vol., ii, 26), who claims that orthonitric acid, $\text{N}(\text{OH})_3$, and other such compounds of nitric acid exist.

According to Erdmann, orthonitric acid, containing 63.63 per cent. of nitric acid, evaporates unchanged at -15° . The authors' experiments do not confirm Erdmann's. About 50 separate experiments were conducted with acids, containing from 61.76 to 77.78 per cent. of nitric acid, which were allowed to evaporate in a current of dry air at -15° and under a pressure of 60 cm. The nitric acid used was prepared by distilling potassium nitrate, and then purified by repeated freezing out from the distillate. Nitric acid melts at -41.3° and not at -47° as Berthelot states. The amounts of acid and of water carried over by the current of air were estimated by direct weighing and by titration with a 0.2*N* borax solution; the results are given in detail and show that an acid containing 63.64 per cent. of nitric acid gives a distillate, under the experimental conditions employed, containing only 54 per cent. of nitric acid. An acid containing 66.1 per cent. of nitric acid gives a distillate of the same strength, whilst the distillates from acids of higher concentration are more concentrated than the acids themselves.

According to Erdmann, the high viscosity exhibited by the compound $\text{O}[\text{N}(\text{OH})_4]_2$ is in accordance with its high molecular weight. It is pointed out that conclusions as to the molecular weight of compounds cannot be drawn from their viscosity constants. Besides, the

experiments quoted show that an acid containing 65 per cent. of nitric acid possesses the greatest viscosity coefficient at $+15^{\circ}$ and -15° , and not an acid containing 70 per cent. of nitric acid and corresponding with Erdmann's hypothetical compound. The authors' viscosity determinations are in accordance with those of Graham. Erdmann quotes -39° as the melting point of his compound, $O[N(OH)_4]_2$. A mixture corresponding with $2HNO_3, 3H_2O$ does not, however, exhibit a sharp melting point. Crystals begin to separate at -39° ; when those, however, are separated from the mother liquor, they melt at -19° and have a composition corresponding with the trihydrate, $HNO_3, 3H_2O$. Erdmann's tribasic acid, $NO(OH)_3$, is the hydrate, HNO_3, H_2O . Erdmann's tetrabasic acid, $O[NO(OH)_2]_2$, does not exist.

The complete freezing point curve of mixtures of water and nitric acid has been determined. The measurements were conducted in a Beckmann apparatus with a thermo-element of nickel and iron and a Deprez-D'Arsonval galvanometer. The solidification temperatures of nitric acid, from 0 to 100 per cent., are quoted. The curve represented shows that nitric acid forms two hydrates, $HNO_3, 3H_2O$ and HNO_3, H_2O , corresponding with 53.84 and 77.77 per cent. by weight of nitric acid respectively. The former hydrate melts at -18.5° , the latter at -38.0° , whilst Pickering gives -18.2° and -36.8° . The curve possesses three minima, indicating the existence of three cryohydrates: at -43° , ice and $HNO_3, 3H_2O$; at -42° , $HNO_3, 3H_2O$ and HNO_3, H_2O ; at -66° , HNO_3, H_2O and HNO_3 .

Conductivity measurements of mixtures of nitric acid and water at -16° were made. The curves show that Erdmann's views are incorrect. The hydrates $HNO_3, 3H_2O$ and HNO_3, H_2O exist in solution at -16° , the former being more stable than the latter. Dilatometric measurements were also made. The lowering of the freezing point caused by the addition of one of the components of dissociation of the monohydrate was measured, the monohydrate dissociating according to the scheme $HNO_3, H_2O \rightleftharpoons HNO_3 + H_2O$. The lowering of the freezing point of the monohydrate by picric acid and of the trihydrate by acetic acid was measured. A. McK.

Formation of Nitrites and Nitrates by the Electrolytic Oxidation of Ammonia in the presence of Copper Hydroxide. WILHELM TRAUBE and ARTHUR BILTZ (*Ber.*, 1904, 37, 3130—3138).—It has been shown by Schönbein that copper is oxidised when immersed in an aqueous solution of ammonia in contact with air, whilst the ammonia is also oxidised to ammonium nitrite. The authors have studied the oxidation of ammonia by oxygen evolved electrolytically and have used copper hydroxide as a catalyser.

Practically no nitrite is formed at the anode when an aqueous solution of sodium hydroxide containing ammonia is electrolysed; when copper hydroxide, however, is added to such a solution, almost the whole of the oxygen evolved at the anode is used up in converting the ammonia present into ammonium nitrite. Platinum or iron electrodes were used in the experiments quoted, and the current strength varied from 5 to 15 amperes.

As the electrolysis proceeds, the amount of nitrite formed gradually increases, and then, after a certain time, decreases owing to the oxidation to nitrate; if the electrolysis be continued for a considerable time, the liquid at the anode is found to contain only nitrate and no nitrite.

A. McK.

A Reagent for Phosphorus, Arsenic, or Antimony Hydride.

PAUL LEMOULT (*Compt. rend.*, 1904, 139, 478—480).—When hydrogen phosphide is passed into a solution of mercuric iodide containing potassium iodide ($\text{HgI}_2, n\text{KI}$, with $n > 2$), an orange-yellow, crystalline solid is formed which becomes brick-red when dry, has the composition PHg_3I_3 , is decomposed slowly by hot or cold water, more rapidly by alkalis, forming an iodide and a black powder, which in its turn breaks down into hydrogen phosphide, mercury, and an alkali phosphite; nitric acid or aqua regia decomposes the compound readily, the former giving a mercury idonitrate, HgINO_3 , and phosphoric acid; the latter liberating iodine and yielding phosphoric acid and a mercury salt.

Similar characteristic compounds are obtained when arsenic or antimony hydride replace the hydrogen phosphide in the above reaction, the arsenic compound having a brown, and the antimony a brownish-black, colour. Ammonia only reacts with concentrated solutions of the reagent, giving the compound $\text{HgI}_2 \cdot 2\text{NH}_3$, in beautiful, crystalline needles 1 cm. long (compare François, *Abstr.*, 1899, ii, 657).

M. A. W.

Preparation of Phosphorus Tribromide. ANASTASIOS C. CHRISTOMANOS (*Zeit. anorg. Chem.*, 1904, 41, 276—290. Compare this vol., ii, 614).—Details of the method of preparing phosphorus tribromide by the action of bromine on yellow phosphorus under a layer of benzene are given. Phosphorus tribromide boils at 171° (corr.) under 761 mm. pressure and melts at -41.5° under 761 mm. pressure. It has $n_D = 1.6945$ at 19.5° , and the sp. gr. 2.88467 at $0^\circ/4^\circ$, 2.85234 at $15^\circ/4^\circ$, and 2.82053 at $27^\circ/4^\circ$. When a current of oxygen is passed into boiling phosphorus tribromide, the action, represented by $4\text{PBr}_3 + 5\text{O}_2 = 2\text{P}_2\text{O}_5 + 6\text{Br}_2$, takes place.

A lecture experiment illustrating the action of water on phosphorus tribromide is described. The action on it of absolute alcohol, phenol, glycerol, copper nitrate, sodium, and magnesium respectively is also described.

A. McK.

Direct Separation, without Liquefaction, of the most Volatile Gases of the Air. Sir JAMES DEWAR (*Ann. Chim. Phys.*, 1904, [viii], 3, 12—20).—Taking advantage of the selective absorptive power exhibited by wood charcoal towards gases (compare this vol., ii, 652), the author has separated the oxygen and nitrogen from the more volatile gases of the air; the unabsorbed residue from 200 c.c. of air showed, when spectroscopically examined, the *C* and *F* lines of hydrogen, the yellow and some orange lines of neon, and the yellow and green lines of helium. By this method, also, the presence of helium has been detected in the gases from the mineral waters of

Bath, of neon in the gases from London water and sea water, and of neon and hydrogen in the gases dissolved in petroleum. M. A. W.

Formation of Helium from the Radium Emanation. F. HIMSTEDT and GEORG MEYER (*Ann. Physik*, 1904, [iv], 15, 184—192).—The most stringent precautions (for example, heating for 20—30 minutes in a vacuum at a bright red heat) have been taken to free the radium preparations from any occluded helium, but in spite of these it appears that fresh helium is produced from the radium preparations after a longer or shorter interval (compare Ramsay and Soddy, *Abstr.*, 1903, ii, 622; Dewar and Curie, this vol., ii, 255).

J. C. P.

Liquefaction of Helium. Sir JAMES DEWAR (*Compt. rend.*, 1904, 139, 421—422).—When a tube full of hydrogen and connected with a side-tube containing wood charcoal (compare this vol., ii, 652) is cooled in liquid hydrogen, the hydrogen is absorbed by the charcoal, producing a vacuum of so high an order that an electric discharge in the tube is impossible; when the tube of hydrogen is replaced by one of helium and cooled to 15° absolute, a coil, capable of producing a spark 40 cm. long in air, only causes an intermittent phosphorescence in the middle of the tube. The author concludes from his experiments that the boiling point of helium is about 6° absolute.

M. A. W.

Actinium. ANDRÉ DEBIERNE (*Compt. rend.*, 1904, 139, 538—540).—Experimental observations are cited which indicate that Giesel's emanium (compare *Abstr.*, 1903, ii, 193) is identical with actinium. The elements associated with each are the same, the phosphorescence phenomena are identical, and so are the time constants of the decay of the induced activity. As a result of fractionating the rare earths by means of the double nitrates which the rare earth metals form with manganese, it is found that the actinium accumulates in the neodymium and samarium fractions, the lanthanum fraction being almost inactive.

H. M. D.

Evolution of Structure in Metals. G. CARTAUD (*Compt. rend.*, 1904, 139, 428—430).—From an examination of the etch figures obtained by the action of picric acid in acetone solution on the polished surface of such metals as zinc, tin, or lead, the author concludes that the final crystalline structure of the metal is evolved from a primitive cellular structure.

M. A. W.

Electrolysis of Alkali Chlorides, using Iron Plates over which Mercury Flows. WILHELM KETTEMBIEL and C. F. CARRIER, jun. (*Zeit. Elektrochem.*, 1904, 10, 561—568).—The cathode consists of an amalgamated iron plate over which mercury is allowed to flow in a thin sheet. It is very difficult to amalgamate the iron properly, and the prepared plate must be preserved with a current flowing to it, otherwise it oxidises very rapidly. The yield of alkali metal obtained increases rapidly with the current density up to about 0.35 ampere

per sq. cm. When the anode is enclosed in a porous pot, the yield of metal is from 85 to 90 per cent. of the theoretical value, but without a diaphragm it is much smaller. The potassium amalgam obtained contained from 1 part of potassium in 6000 of mercury to 1 part in 30,000. Within these limits, the yield is hardly affected by the rate of flow of the mercury. T. E.

Ammonia Soda Process from the Standpoint of the Phase Rule. P. P. FEDOTÉEFF (*Zeit. physikal. Chem.*, 1904, 49, 162—188).—The ammonia soda process has to be considered under the category of reciprocal salt pairs, the four salts involved being sodium and ammonium chlorides and hydrogen carbonates. To furnish the experimental data required for such a study, the author has determined the solubility of each of the above salts in presence of each of the others at various temperatures up to 45°, a lower temperature, however, being prescribed in some cases by the limited stability of ammonium hydrogen carbonate. The solutions were in all cases saturated with carbon dioxide. Further, the author has studied both at 0° and 15° the composition (1) of a saturated solution in contact with the solid phase $\text{NaHCO}_3 + \text{NH}_4\text{Cl} + \text{NH}_4\text{HCO}_3$; (2) of a saturated solution in contact with the solid phase $\text{NaHCO}_3 + \text{NH}_4\text{Cl} + \text{NaCl}$. The solution (1) is an incongruent saturated solution (see Meyerhoffer, *Abstr.*, 1896, ii, 414), that is, although ammonium hydrogen carbonate is present in the solid form, there is none of it in the solution, which contains sodium chloride instead (this does not hold, however, above 32°). Addition of excess of sodium chloride to solution (1) changes it into solution (2), which is a congruent saturated solution. It appears that a congruent saturated solution is obtained when the radicle present in the solution in the greatest concentration is twice represented among the three solid salts.

The results are represented in the usual graphical manner, and without reference to the diagrams, the author's deductions cannot be fully explained. It is possible to deduce the way in which, and the extent to which, the yield of solid sodium hydrogen carbonate is affected by changing the temperature or the concentration of the solutions, and also the maximum yield that may be expected under given conditions. It is theoretically possible to precipitate about 80 per cent. of the sodium chloride taken in the form of hydrogen carbonate, and a yield of 75 per cent. should be practically obtainable. From the purely chemical standpoint, Solvay's method is not to be regarded as the best form of the ammonia soda process. It would appear to be more rational to start from solid or dissolved sodium chloride and solid ammonium hydrogen carbonate. J. C. P.

Borax of Abnormal Composition. LEOPOLD SPIEGEL (*Chem. Zeit.*, 1904, 28, 750—751).—A sample of borax examined by the author gave unusual results on titration with *N*/5 sulphuric acid, using *p*-nitrophenol as indicator. This sample, on further investigation, was found to consist of sodium triborate. As the result of a considerable number of experiments, it was ascertained that solutions of borax (diborate) containing excess of boric acid deposit crystals of

sodium triborate. Many samples of commercial borax were examined, but, with the above exception, all consisted of sodium diborate, showing that the triborate seldom occurs.

W. P. S.

Silver Chromate. I. BENJAMIN M. MARGOSCHES (*Zeit. anorg. Chem.*, 1904, 41, 68—84).—Silver chromate, Ag_2CrO_4 , is best prepared by interaction of an easily soluble silver salt and a normal chromate, when it is precipitated as an indistinctly crystalline powder. The chromate is also formed in dark green crystals by the action of an excess of water on silver dichromate. Other methods of preparation are quoted. Data quoted in the literature respecting the solubility of silver chromate in water are very discordant.

Silver chromate dissolves in ammonia of sp. gr. = 0.94, to form the compound $\text{Ag}_2\text{CrO}_4 \cdot 4\text{NH}_3$. The interaction between alkali haloids and silver chromate proceeds only with freshly precipitated or moist silver chromate. Silver chromate is slightly soluble in a concentrated solution of potassium chromate; it is practically insoluble in silver nitrate solution. The data in the literature respecting the behaviour of silver chromate towards nitric acid are also at variance.

A. McK.

Solubility of Calcium Sulphate in Solutions of Nitrates. ATHERTON SEIDELL and JOSEPH G. SMITH (*J. Physical Chem.*, 1904, 8, 493—499).—The solubility is given in grams per litre, and the densities of the solutions are also recorded. In solutions of sodium nitrate, the solubility reached a maximum (9.3 grams per litre) for about 300 grams of sodium nitrate per litre, after which it decreased. In solutions of potassium nitrate, the results were complicated by the formation of syngenite at higher concentrations of the nitre. In solutions of magnesium nitrate, the solubility steadily increases, so that for 514 grams of magnesium nitrate per litre it reaches over 15 grams per litre, that is, over seven times the solubility in pure water. In solutions of calcium nitrate, the solubility decreases. Tables and curves of the results are given.

L. M. J.

Electrolytic Preparation of Calcium. OTTO RUFF & WILHELM PLATO (D.R.-P. 153731).—The best results in the electrolytic preparation of calcium are obtained by employing a bath consisting of 83.5 per cent. of calcium chloride and 16.5 per cent. of calcium fluoride, melting at 655° and having a sp. gr. 2.5. A carbon anode and an iron cathode are employed.

C. H. D.

Action of Carbon Dioxide on Magnesium Hydroxide. M. MONHAUPT (*Chem. Zeit.*, 1904, 28, 868).—When a current of carbon dioxide is passed through water in which magnesium hydroxide is suspended, a liquid is obtained containing a varying amount of magnesium oxide. In three experiments, the author obtained, respectively, 10.7, 9.7, and 11.3 per cent. By prolonged heating at 50 — 60° , or by adding an equal volume of alcohol, carbon dioxide is gradually evolved and a precipitate is obtained having the composition $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$.

The portion not dissolved by the water also has the same composition, but it obstinately retains some 3·7 per cent. of unchanged magnesium hydroxide.

L. DE K.

Zinc-magnesium Alloys. OCTAVE BOUDOUARD (*Compt. rend.*, 1904, 139, 424—426. Compare Abstr., 1901, ii, 512; 1902, ii, 141, 501; 1903, ii, 78, 480).—The melting points of a series of mixtures of zinc and magnesium containing from 5 to 90 per cent. of magnesium show a maximum (570°) and two minima (355° and 332°); the maximum represents the melting point of the compound Zn_2Mg , which can be isolated in the form of a metallic powder by the prolonged action in the cold of 0·3 per cent. hydrochloric acid solution on the mixture containing 80 per cent. of zinc. A second compound, ZnMg , can be similarly isolated by the action of a warm 0·5 per cent. solution of ammonium chloride on the mixture containing 30 per cent. of zinc. The alloys of zinc and magnesium are white in colour, more or less bright, and their brittleness increases with the proportion of zinc; the alloy containing 10 per cent. of zinc can be sawn and filed, whilst those containing 50—90 per cent. break in the process of sawing.

M. A. W.

Deposition of Zinc from Zinc Chloride dissolved in Acetone. HARRISON EASTMAN PATTEN (*J. Physical Chem.*, 1904, 8, 483—487).—A curve is given for current density (between electrodes 3 sq. cm. in area) and *E.M.F.* The results show that a residual current is obtained in which the curve is almost a straight line; at about 2 volts, however, the curve bends to give the true *C/E.M.F.* curve. This is a straight line, which indicates a specific conductivity of $2\cdot99 \times 10^{-2}$ at $20\cdot5^{\circ}$ and a polarisation *E.M.F.* of 1·90 volts; or, if the latter be taken from the intersection of the two straight line portions of the curve, of 2·14 volts. The zinc can be deposited steadily with a current density as low as 2 amperes per square foot, and at 40 amperes per square foot it trees out at the edges. When the thickness of the coating reaches about 1 mm., the deposit becomes spongy. The deposit was further found to contain about 1 per cent. of carbon.

L. M. J.

Phosphorescent Zinc Sulphide. H. GRÜNE (*Ber.*, 1904, 37, 3076—3077).—Pure zinc sulphide is not phosphorescent, but the addition of a trace of copper, silver, lead, bismuth, tin, uranium, or cadmium causes it to become so. Copper produces the best result, 1 part of copper in 10,000 causing a beautiful green phosphorescence. The addition of manganese, on the other hand, produces a yellowish-red phosphorescence, and the zinc sulphide in this case, when scratched or rubbed, emits light spontaneously.

W. A. D.

Glowing of Sidot's Blende under the Influence of Ozone. RUDOLF SCHENCK and F. MIHR (*Ber.*, 1904, 37, 3464—3467).—Hexagonal zinc sulphide, Sidot's blende, glows intensely under the influence of a small amount of ozonised oxygen and also scintillates. The

blende scintillates feebly when kept in a dark room removed from all radioactive substances and from ozone. J. J. S.

Solubility of Copper Oxide, Hydroxide, and Carbonate in Ammonia. ERNST MURMANN (*Chem. Centr.*, 1904, ii, 410; from *Oesterr. Chem. Zeit.*, 7, 272).—In preparing an ammoniacal solution of copper hydroxide, it was found that only a portion of it dissolved even in presence of a large excess of ammonia, but when a quantity of ammonium carbonate or other ammonium salt equal to about half the copper compound was added, the whole of the latter went into solution. Pure calcined copper oxide is very sparingly soluble in ammonia, but considerably more so in presence of ammonium salts. E. W. W.

Complex Hydroxides of Copper, Nickel, Cadmium, Zinc, and Silver with Ammonia. W. BONSDORFF (*Zeit. anorg. Chem.*, 1904, 41, 132—192).—Copper hydroxide, prepared by the action of sodium hydroxide on copper ammonium sulphate, was dissolved in ammonia, the excess of which was removed in a vacuum over sulphuric acid. The hydroxides of nickel, cadmium, and zinc were acted on by ammonia in a similar manner. Potential measurements were made by Bodländer's method at 25° as contrasted with the normal electrode, $\text{Hg} \mid \text{HgCl}$ and $N\text{KCl}$ solution. Experiments with copper and nickel were unsuccessful. Difficulties were encountered in the preparation of constant electrodes, which were obtained, however, from potassium zinc cyanide with a little mercury.

The complex cation of cadmium ammonium hydroxide is represented by $\text{Cd}_m(\text{NH}_3)_{4m}$, whilst the cation with zinc ammonium hydroxide is $\text{Zn}_m(\text{NH}_3)_{3m}$.

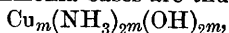
Measurements of the electrical conductivity of copper hydroxide in ammonia show that, when the concentration of ammonia is small, one or more copper ammonia bases are present in solution. Comparison of the conductivity curves of copper hydroxide and ammonia with the corresponding curves of barium hydroxide and ammonia indicate that from concentrations of ammonia exceeding 3—4 *N* onwards a somewhat strong copper ammonia base is present in the solution. The number of ammonia molecules in this strong base is greater than with the weaker bases, being probably greater than 4. Conductivity measurements of nickel and cadmium hydroxides and of silver oxide in ammonia show that they form strong bases with ammonia.

From conductivity measurements of solution of zinc hydroxide in ammonia, it follows that zinc hydroxide, in contradistinction to cadmium hydroxide, forms very weak ammonia bases.

Measurements of the concentration of hydroxyl ions by Koelichen's method corroborate the result of the conductivity determinations in the cases of solutions of copper and zinc in ammonia.

Determinations of the solubility of copper, nickel, cadmium, and zinc hydroxides respectively in ammonia show that the hydroxides in question easily suffer changes, but it is difficult to obtain well-defined modifications. When the excess of ammonia is small, 1 atom of copper combines with 2NH_3 , whilst 1 atom of cadmium or of nickel combines with 4NH_3 .

The complex copper ammonia bases are thus constituted,



whilst the nickel and cadmium ammonia bases have the constitution
 $\text{Ni}_m(\text{NH}_3)_{4m}(\text{OH})_{2m}$ and $\text{Cd}_m(\text{NH}_3)_{4m}(\text{OH})_{2m}$. A. McK.

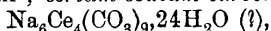
Metallic Nitroso-compounds. VOLKMAR KOHLSCHÜTTER and M. KUTSCHEROFF (*Ber.*, 1904, 37, 3044—3052).—The amount of nitric oxide absorbed by cupric chloride solutions diminishes as the solution is diluted with water, but, on the other hand, increases rapidly when strong hydrochloric acid is used as the diluent. The amount of nitric oxide absorbed per molecule of cupric chloride in methyl- or ethyl-alcoholic solutions at first increases and finally decreases again as the solutions are diluted. In acetone solutions, very much more nitric oxide is absorbed, and the amount increases on dilution, a similar increase being manifested by solutions in formic acid. E. F. A.

Dissociation of Copper Sulphate and Decomposition of Copper Anodes. DONATO TOMMASI (*Chem. Centr.*, 1904, ii, 180; from *Electrochem. Zeit.*, 11, 56—57).—When a chemically pure copper sulphate solution is boiled, a basic salt is deposited which, when subsequently left to itself in the cold for 24 hours, does not dissolve to any great extent; the more concentrated the copper sulphate solution, the more strongly basic is the deposit. Even at the ordinary temperature, a copper sulphate solution decomposes appreciably in the course of a year. These observations may explain the deposit that appears at a copper anode during the electrolysis of copper sulphate or dilute sulphuric acid. J. C. P.

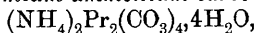
The Rendering Active of Oxygen. X. Autoxidation of Cerous Salts. CARL ENGLER (*Ber.*, 1904, 37, 3268—3273. Compare Abstr., 1903, ii, 599; this vol., ii, 165, and Baur, Abstr., 1903, ii, 729; this vol., ii, 339).—The large absorption of gas (oxygen) observed by Baur is due to carbon dioxide present in the gas. This carbon dioxide is formed when the carbonate solution is treated with acid to form the hydrogen carbonate, and if care is not taken is transferred to the absorbing vessel. In all cases, the amount of peroxide formed agrees with the ratio 1 mol. of oxygen for 2 atoms of cerium, and the absorption confirms this if all carbon dioxide is first removed. J. J. S.

Preparation of the Cerium Earths by Aid of their Alkali Double Carbonates. RICHARD J. MEYER (*Zeit. anorg. Chem.*, 1904, 41, 97—125).—The following alkali double carbonates were prepared and analysed: *lanthanum potassium carbonate*, $\text{K}_2\text{La}_2(\text{CO}_3)_4 \cdot 12\text{H}_2\text{O}$, formed by the gradual addition of an aqueous solution of lanthanum chloride to an aqueous solution of potassium carbonate and then crystallising the resulting precipitate, forms silky crystals; *lanthanum sodium carbonate*, $\text{Na}_6\text{La}_4(\text{CO}_3)_9 \cdot 20\text{H}_2\text{O}$ (?), is gelatinous; *lanthanum ammonium carbonate*, $(\text{NH}_4)_2\text{La}_2(\text{CO}_3)_4 \cdot 4\text{H}_2\text{O}$, is crystalline; *cerium*

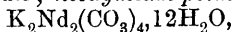
potassium carbonate, $\text{K}_2\text{Ce}_2(\text{CO}_3)_4 \cdot 12\text{H}_2\text{O}$, assumes a faintly yellow colour on exposure to air; *cerium sodium carbonate*,



is amorphous; *cerium ammonium carbonate*, $(\text{NH}_4)_2\text{Ce}(\text{CO}_3)_4 \cdot 6\text{H}_2\text{O}$, forms tiny crystals and assumes a yellow colour on exposure to air; *praseodymium potassium carbonate*, $\text{K}_2\text{Pr}_2(\text{CO}_3)_4 \cdot 12\text{H}_2\text{O}$, crystallises in tiny needles; *praseodymium sodium carbonate*, $\text{Na}_6\text{Pr}_4(\text{CO}_3)_9 \cdot 22\text{H}_2\text{O} (?)$, is amorphous; *praseodymium ammonium carbonate*,



forms bright green crystals; *neodymium potassium carbonate*,



forms needles grouped in rosettes; *neodymium sodium carbonate*, $\text{Na}_6\text{Nd}_4(\text{CO}_3)_9 \cdot 4\text{H}_2\text{O}$, crystallises in prisms; *neodymium ammonium carbonate*, $(\text{NH}_4)_3\text{Nd}_2(\text{CO}_3)_4 \cdot 4\text{H}_2\text{O}$, forms regular prisms. The constitution of the sodium salts given is not so certain, owing to the ease with which they are decomposed. Whilst the ammonium and sodium salts described are soluble with great difficulty in solutions of the corresponding alkali carbonates, the potassium salts are easily soluble in concentrated potassium carbonate solution, although the degree of solubility in the case of the compounds of the four rare metals examined is very different; thus the double carbonates are precipitated by the addition of water to their concentrated solutions in the following sequence: lanthanum, praseodymium, cerium, and neodymium. Lanthanum can accordingly be almost completely separated from cerium and didymium by precipitating as the double carbonate several times.

Traces of cerium can be detected by the yellow coloration formed in solutions of its alkali carbonates by peroxidation.

Praseodymium oxide, containing traces of cerium, neodymium, and lanthanum, can be completely freed from cerium and neodymium by the potassium carbonate method, whilst lanthanum can be removed almost entirely by systematic crystallisation of the praseodymium oxalate from nitric acid.

Praseodymium peroxide, $4\text{PrO}_2 \cdot \text{Pr}_2\text{O}_3$, is obtained by heating praseodymium oxalate to a low red heat, whilst the oxide, PrO_2 , is obtained by Brauner's method by heating a mixture of praseodymium nitrate and potassium nitrate at $400-450^\circ$.

The pure praseodymium suboxide, Pr_6O_{11} , could not be oxidised to PrO_2 by means of cerium dioxide.

The separation of pure praseodymium from a solution in citric acid could not be effected by Baskerville and Turrentine's method (this vol., ii, 261).

A. McK.

Light Aluminium Alloys. JOSEPH W. RICHARDS (*Chem. Centr.*, 1904, ii, 297; from *J. Franklin Inst.*, 157, 394—395).—From a lecture given by the author. The effects of alloying aluminium with chromium, manganese, copper, nickel, tin, silver, tungsten, and zinc are described.

J. C. P.

Artificial Production of Rubies by Fusion. AUGUSTE VERNEUIL (*Ann. Chim. Phys.*, 1904, [viii], 3, 20—48).—Artificial rubies

in the form of spheroids having a diameter of 5 to 6 mm. and weighing 2.5 to 3 grams (12 to 15 carats) can be obtained by allowing a blow-pipe flame, rich in hydrogen or carbon, to play on the extremity of a small cylinder of alumina, while a mixture of alumina and 2.5 per cent. of chromium oxide in the form of a powder is mechanically blown with the oxygen into the tube of the blow-pipe, and thus deposited on the surface of the fused mass of alumina. The artificial stones thus obtained are identical in physical and crystallographical properties with the natural gems, from which, however, they can be detected by the presence of minute bubbles visible only under the microscope.

M. A. W.

Aluminium Hydroxide. I. FRANZ RUSS (*Zeit. anorg. Chem.*, 1904, 41, 216—230).—The conditions were determined under which solutions of sodium aluminate decompose with the formation of the crystalline variety of aluminium hydroxide; these conditions depend on the ratio $\text{Al}_2\text{O}_3 : \text{Na}_2\text{O}$, on the temperature, and on the concentration.

Whilst solutions of sodium aluminate of the type $\text{Al}_2\text{O}_3 : \text{Na}_2\text{O} = 1 : 3$ are very stable, the decomposition begins when this ratio sinks below 1 : 2. The formation of the crystalline hydroxide is favoured by low temperatures. In order to determine the dependence of the spontaneous decomposition of a solution of known composition on its concentration, solutions of the type $\text{Al}_2\text{O}_3 : \text{Na}_2\text{O} = 1 : 1.24$ were examined in different concentrations. The crystalline variety of aluminium hydroxide does not separate when the density of the sodium aluminate solution is below 1.17; with solutions where the density is below 1.17, colloidal alumina is first formed, and this, in the course of time, is transformed into the crystalline modification.

The existence of two hydroxides is assumed, the β -variety being the more stable, and its transformation from the α -variety is accelerated by the presence of hydroxyl ions. The β -variety is practically insoluble in *N*-sulphuric acid at the ordinary temperature. The solubility of the β -hydroxide in solutions of sodium hydroxide of varying concentrations increases with increase of hydroxyl ions.

From the results obtained, the most favourable conditions are indicated under which aluminium hydroxide can be obtained from sodium aluminate solutions according to Baeyer's process.

A. McK.

"Ageing" of Clays. PAUL ROHLAND (*Zeit. anorg. Chem.*, 1904, 41, 325—336).—Such substances as form colloidal solutions with water possess plasticity to a greater or less degree. Clay and porcelain contain such colloidal substances, the union of which with water to form aluminium silicate is the cause of the plasticity; the degree of plasticity is expressed by the ratio of the inactive amount to the active mass. The coagulation of these colloids may be accelerated by catalysts, this acceleration being a function of the hydrogen and hydroxyl ions. The increase of the degree of plasticity during the "ageing" is accounted for as follows: the hydroxyl ions of the solutions in contact with the clay are neutralised by the fermentation of the organic substances present; excess of hydrogen ions results and coagulation

ensues. The degree of plasticity of clays may be increased by the addition of colloids, such as tannic acid, dextrin, or aluminium hydroxide. A. McK.

Nature of the Alkaline Solution of Chromium Hydroxide. WALTER HERZ (*Chem. Centr.*, 1904, ii, 178).—Kremann's objections (Abstr., 1903, ii, 54, 465) to regarding the alkaline solution of chromium hydroxide as a colloidal solution are criticised (compare also Fischer and Herz, Abstr., 1902, ii, 564; Bredig, Abstr., 1903, ii, 263). The chrome alum used by Kremann for his dialysis experiments contained chromium-sulphuric acids, and was therefore unsuitable. If green chromium chloride is used, no dialysis takes place in 36 hours, even with alkali in the outer vessel. J. C. P.

The Action of Nitric Oxide on Chromous Salts. VOLKMAR KOHLSCHÜTTER (*Ber.*, 1904, 37, 3053—3055. Compare Chesneau, Abstr., 1899, ii, 661).—When saturated with nitric oxide, chromous salts give brilliant red solutions. Apparently, when chromous salt solutions absorb nitric oxide, this is reduced either to ammonia in neutral solutions or to hydroxylamine in acid solutions. The amount of hydroxylamine in these solutions is unaltered by heating with hydrochloric acid. More chromous chloride is required to convert a given weight of nitric oxide into ammonia than into hydroxylamine. E. F. A.

Ammonium Hydrogen Salt of Chromatodiperacid. KARL A. HOFMANN and H. HIENDLMAIER (*Ber.*, 1904, 37, 3405—3407. Compare this vol., ii, 410).—The action of acetic acid on the ammonium salt of chromatodiperacid leads to the formation of the *ammonium hydrogen* salt, $\text{CrO}_2(\text{O} \cdot \text{O} \cdot \text{NH}_4)(\text{O} \cdot \text{OH})$; this is also obtained when a mixture of a cold saturated ammonium chromate solution and 10 per cent. acetic acid is oxidised with 30 per cent. hydrogen peroxide at 0° . It crystallises in dark reddish-violet, glistening, double refractive prisms, and dissolves in water to a reddish-brown solution, which, on warming, evolves oxygen and finally contains ammonium dichromate. It is less explosive than the diammonium salt when heated or moistened with concentrated sulphuric acid; in the presence of ether, and on addition of dilute sulphuric acid, it forms the blue solution of perchromic acid. With baryta water, barium chloride, and lead acetate solution, it gives coloured precipitates which change into the respective chromates. The *silver* salt is blue by transmitted, scarlet by reflected, light, and is comparatively stable.

On addition of dilute sulphuric acid to the alcoholic solution of the ammonium salts of chromatodiperacid, the solution becomes blue, and, on warming, green, the change being accompanied by oxidation of the alcohol. G. Y.

Unstable and Metastable Equilibria in Iron-Carbon Alloys. E. HEYN (*Zeit. Elektrochem.*, 1904, 10, 491—504).—The effects of hardening and tempering steels with varying quantities of carbon are

studied, mainly by means of micro-photographs. When steel containing less than 0.95 per cent. of carbon is cooled slowly, so that stable equilibrium is attained, it consists entirely of ferrite (pure iron) mixed with perlite. The origin of the perlite is as follows: when the fused steel solidifies, crystals of γ -iron containing carbon in solid solution are deposited; on further cooling, these crystals decompose into β -iron and crystals with a higher percentage of carbon; at a still lower temperature (about 800°), the β -iron changes into α -iron (these are microscopically identical). Finally, at 700° , the solid mass consists of crystals of α -iron mixed with crystals containing 0.95 per cent. of carbon. Below 700° , the latter decompose into a mixture of iron and iron carbide, Fe_3C (cementite), with a very fine-grained structure consisting of alternate layers of the constituents; this mixture is perlite. When the quantity of carbon present exceeds 0.95 per cent., the excess crystallises out as cementite. In slowly cooled steels, therefore, microscopic examination shows ferrite mixed with increasing quantities of perlite up to 0.95 per cent. carbon (this mixture consists entirely of perlite) and, with more carbon, perlite mixed with increasing quantities of cementite.

When a steel is quickly cooled from a temperature above 700° , however, the stable equilibria are not attained; the greater the rate of cooling, the more completely are the constituents which exist at the high temperature preserved in the cold steel. In steel containing less than 0.95 per cent. of carbon, the homogeneous mixed crystals will decompose into crystals containing more and less carbon than the original steel, whilst steel containing more than 0.95 per cent. of carbon yields mixed crystals containing less carbon than the original material and crystals which approach more nearly to cementite the more slowly the cooling takes place. The author proposes to retain the name martensite for all these partially decomposed mixtures, instead of giving the constituent which most nearly approaches cementite the special name austenite. The author's experience of the properties of austenite is not entirely in accord with that of Osmond.

Osmond's view that troostite is a product intermediate between martensite and perlite is confirmed. Very rapid cooling gives martensite, somewhat less rapid cooling yields troostite, whilst slow cooling leads to perlite. If a rectangular piece of steel is quenched in water, the corners (which are most rapidly cooled) consist of martensite, the internal portions being troostite. When tempered, both troostite and martensite pass into "sorbite," which appears to be an almost molecular mixture of ferrite and a substance resembling cementite. The presence of a little manganese diminishes the tendency to form troostite, in other words, it makes super-cooling easier.

In the diagram of Roberts-Austen and Bakhuis Roozeboom (this vol., ii, 717), fused iron containing less than 4.3 per cent. of carbon is supposed to deposit iron-carbon mixed crystals; with more than 4.3 per cent. of carbon, graphite is deposited, the eutectic (mixed crystals and graphite) lying at 4.3 per cent. carbon and about 1100° . But since the solid iron does not contain any graphite, it is assumed by Bakhuis Roozeboom that below 1100° the mixed crystals react with

graphite to produce carbide (cementite). The author points out that this view cannot be reconciled with the well-established fact that white cast-iron is obtained by rapid cooling, whilst slow cooling produces grey cast-iron, and, further, that when white cast-iron is heated graphite is set at liberty. The author suggests that the graphite is probably the constituent which corresponds with the condition of stable equilibrium, but, in consequence of super-cooling, the fused iron may readily cool below the temperature at which graphite should crystallise out and reach the somewhat lower temperature at which carbide crystallises. The carbide would then represent a metastable equilibrium which is reached only on account of a considerable retardation of the crystallisation of the graphite. This view is in accordance both with Roberts-Austen's experimental results and with metallurgical experience. Silicon diminishes the tendency to super-cooling, manganese increases it.

T. E.

Properties and Constitution of Chromium Steels. LÉON GUILLET (*Compt. rend.*, 1904, 139, 426—428).—The connection between the micrographical properties and the composition of the chromium steels examined is shown in the following table :

| Class. | Microstructure. | Steels containing | |
|--------|-------------------------|---------------------------|---------------------------|
| | | 0·2 per cent. of carbon. | 0·8 per cent. of carbon. |
| 1 | Perlite..... | 0—7 per cent. of chromium | 0—5 per cent. of chromium |
| 2 | Martensite or troostite | 7—15 „ „ | 5—10 „ „ |
| 3 | Martensite and carbide | 15—20 „ „ | 10—18 „ „ |
| 4 | Carbide | more than 20 „ „ | more than 18 „ „ |

In respect of their mechanical properties, the steels containing the double carbide are too brittle for industrial purposes, whilst of all the martensite steels so far examined (compare Abstr., 1903, ii, 297, 650, 730 ; this vol., ii, 266) those containing chromium are the hardest.

The chief mechanical properties of the chromium steels are tabulated in the original.

M. A. W.

Constitution and Properties of Tungsten Steels. LÉON GUILLET (*Compt. rend.*, 1904, 139, 519—521).—Tungsten steels, containing 0·2 per cent. of carbon, show perlite or carbide structure according as the percentage of tungsten is less or greater than ten. In the case of steels containing 0·8 per cent. of carbon, the change in structure appears with 5 per cent. of tungsten. The breaking weight of the perlitic steels increases with the amount of tungsten present, that of the carbide steels decreases. The hardness and fragility of both classes are not much altered by the contained tungsten. Tempering transforms the carbide steels into martensite steels, but carbide is also found after tempering, if much tungsten is present. Certain steels (0·8 per cent. C, > 2 per cent. W). can be tempered by air-cooling.

H. M. D.

Properties and Constitution of Molybdenum Steels. LÉON GUILLET (*Compt. rend.*, 1904, 139, 540—542).—Molybdenum steels,

containing about 0.2 per cent. of carbon, exhibit perlite or carbide structure according as the molybdenum is present in quantity less or greater than 2 per cent. In the case of steels containing about 0.85 per cent. of carbon, the transition from perlite to carbide structure takes place at 1 per cent. of molybdenum. The influence of molybdenum on the properties of the steels is quite similar to that of tungsten (preceding abstract), but larger quantities of the former are required to produce the same effect.

H. M. D.

Action of Arsenious Acid on Freshly-precipitated Iron Hydroxide. WILHELM BILTZ (*Ber.*, 1904, 37, 3138—3150).—Solutions of arsenious acid, containing some potassium chloride, were agitated at the temperature of the laboratory with freshly-precipitated ferric hydroxide and the amount of arsenious acid removed from the solution by the hydrogel determined by titration with standard iodine solution. From the results quoted, it appears that the action of ferric hydroxide as an antidote in arsenical poisoning is due neither to the formation of a basic ferric acetate nor to the formation of a solid solution, but to absorption.

Experiments were conducted with solutions both of vitreous and of crystalline arsenious oxide. The distribution of arsenious acid between water and ferric hydroxide was also measured at 100°. The reversibility of the action was examined by first allowing the equilibrium to be established between the solution of arsenious acid and ferric hydroxide, then separating the liquid in contact with the solid and replacing it by water; the mixture was then agitated for several hours until equilibrium was again attained and the amount of arsenious acid in the liquid estimated as before.

The absorption property of the iron hydrosol during its formation from the hydrosol, obtained by the dialysis of ferric nitrate, was also examined.

Silicic acid and aluminium hydroxide show very slight absorption properties.

The action of antitoxins on the toxins of blood serum is discussed.

A. McK.

Oxidation of Solutions of Ferrous Salts. EDUARD JORDIS [with HUBERT VIERLING] (*Zeit. Elektrochem.*, 1904, 10, 679—682).—Samples of ferrous ammonium sulphate crystallised in large and small crystals and precipitated with alcohol show considerable differences in their conductivity in aqueous solution. The last sample contained 0.153 per cent. of alcohol. There are also small differences in the composition of the samples.

The oxidation of solutions of ferrous salts by air is accelerated by platinum and by small quantities of sulphuric acid. The precipitate which forms in presence of platinum is yellow, it contains 20 equivalents of ferric iron to one equivalent of SO_4 , and is insoluble in cold acids. That formed without platinum is red, contains 16.89 equivalents of iron to one of SO_4 , and dissolves readily in cold acids. A large number of measurements of electrode potentials in more or

less oxidised ferrous salt solutions have been made, but the details are not given. T. E.

Cobalt Chloride. WILLIAM OECHSNER DE CONINCK (*Bull. Akad. Roy. Belg.*, 1904, 6, 803—805).—Anhydrous ethylene glycol dissolves 10.6 per cent. of cobalt chloride hexahydrate at 16.4°, giving a violet-purple solution, which becomes dark blue on heating. Anhydrous cobalt chloride is obtained on distilling this solution under reduced pressure; in a moist atmosphere, it takes up water again, forming first the di- and then the tetrahydrate. E. F. A.

Action of Potassium Nitrite on Nickel Salts. II. III. C. REICHARD (*Chem. Zeit.*, 1904, 28, 885—886, 912).—Further particulars of the various double compounds are given (this vol., ii, 488). The formula for the barium compound is

$$2\text{Ni}(\text{NO}_2)_2\text{Ba}(\text{NO}_2)_2\cdot 2\text{KNO}_2,$$
and the calcium and strontium compounds have a corresponding composition. L. DE K.

Titanium and Tin Compounds. FRIEDRICH EMICH (*Monatsh.*, 1904, 25, 907—912. Compare Ruff and Plato, this vol., ii, 265).—Barium titanifluoride, $\text{BaTiF}_6\cdot\frac{1}{2}\text{H}_2\text{O}$, is obtained as a coarse, crystalline precipitate when barium chloride is added to a hot aqueous solution of potassium titanifluoride; it loses water of crystallisation only on prolonged heating at a dull red heat; when heated more highly, it decomposes with formation of titanium tetrafluoride, which has the properties previously described (*loc. cit.*).

Titanium tetrachloride solidifies at -23° ; stannic iodide boils at 341° (corr.).

Potassium stannifluoride, $\text{K}_2\text{SnF}_6\cdot\text{H}_2\text{O}$, is formed as a crystalline precipitate when stannic chloride is treated with potassium fluoride in warm water; with concentrated sulphuric acid, it evolves hydrogen fluoride.

Barium stannifluoride, $\text{BaSnF}_6\cdot 3\text{H}_2\text{O}$, obtained in the same manner, crystallises in glistening leaflets, and yields hydrogen fluoride when treated with concentrated sulphuric acid. G. Y.

Preparation of Homogeneous Products from Tantalum and other Difficultly Fusible Metals. SIEMENS & HALSKE, AKT.-GES. (D.R.-P. 152848, 152870, and 153826).—Tantalum and other difficultly fusible metals may be fused by means of an electric current, the powdered metal being previously compressed to form rods. The operation is carried out under reduced pressure, an atmosphere of nitrogen or hydrogen not being admissible. In order to prevent the volatilisation of the tantalum, the compressed rod is best made the positive electrode, a comparatively large metallic negative electrode being used, cooled to a temperature only slightly above the melting point of tantalum. Or the cooling surface may be brought into the neighbourhood of the electrodes without being connected with them, but the former plan requires a smaller expenditure of energy.

C. H. D.

Preparation of Colloidal Metals. NICOLA CASTORO (*Zeit. anorg. Chem.*, 1904, 41, 126—131).—When acetaldehyde is added to a hot and faintly alkaline solution of gold chloride, the gold hydrosol is formed, exhibiting colorations, sky-blue, amethyst, violet, pink, or purple, varying with the particular dilution. A gold mirror may be obtained under suitable conditions. When a 1 per cent. solution of gold chloride is heated with 1 c.c. of allyl alcohol, a faintly violet coloration is first produced, which changes to a ruby-red. Such concentrated solutions of gold hydrosol do not deposit gold after being dialysed during ten days.

The hydrosols of platinum, palladium, osmium, and ruthenium may also be prepared from the chlorides of the metals by means of acetaldehyde. A. McK.

Densities of Alloys of Gold and Copper and of Gold and Silver. COPIUS HOITSEMA (*Zeit. anorg. Chem.*, 1904, 41, 63—67).—The following values were obtained with alloys of gold and copper:

| Gold in 0/00. | Sp. gr. at 15°. | Specific volume. |
|---------------|-----------------|------------------|
| (1000) | (19·26) | (0·05192) |
| 917 | 17·35 | 0·05764 |
| 833 | 15·86 | 0·06305 |
| 750 | 14·74 | 0·06784 |
| 583 | 12·69 | 0·07880 |
| 250 | 10·035 | 0·09965 |
| 0 | (8·7) | (0·11494) |

With alloys of gold and silver the results were:

| Gold in 0/00. | Sp. gr. at 15°. | Specific volume. |
|---------------|-----------------|------------------|
| (1000) | (19·26) | (0·05192) |
| 917 | 18·08 | 0·05531 |
| 843 | 16·96 | 0·05896 |
| 750 | 16·03 | 0·06238 |
| 667 | 15·07 | 0·06636 |
| 583 | 14·24 | 0·07023 |
| 500 | 13·60 | 0·07353 |
| 417 | 13·00 | 0·07692 |
| 333 | 12·38 | 0·08070 |
| 250 | 11·78 | 0·08489 |
| 167 | 11·28 | 0·08861 |
| 0 | (10·4) | (0·09569) |

A. McK.

Analysis of Margules' Platinum Sulphate. LEO STUCHLIK (*Ber.*, 1904, 37, 2913—2915).—The solution of platinum in sulphuric acid of sp. gr. 1·840, obtained by Margules (*Abstr.*, 1898, ii, 497) by means of an alternating current, deposits yellow crystals, which retain free sulphuric acid even after several crystallisations from water. By repeated crystallisation from water in a vacuum, large, orange leaflets of $\text{Pt}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ are obtained. The salt loses water in a desiccator,

becoming darker in colour. The anhydrous salt shows green metallic reflex. The salt containing sulphuric acid is stable, losing little in weight at 100° and remaining orange in colour. Both salts dissolve readily in water, the hydrated salt to a yellow and the anhydrous salt to a dark solution. The yellow solution deposits a brown, basic salt on warming (compare Ruer, Abstr., 1903, ii, 407). Sulphuric acid precipitates yellow crystals, apparently of the hydrated salt, from the dark solution.

C. H. D.

Mineralogical Chemistry.

Radioactive Cinnabar. SIMA M. LOSANITSCH (*Ber.*, 1904, 37, 2904—2906).—Specimens of cinnabar from Avala and Bare in Servia, and Idria in Austria, were found to be radioactive, although much less so than pitchblende. Other mercury minerals examined were inactive. The barytes which accompanies the active cinnabar is inactive, from which it is concluded that radium is absent and that the activity is due to a “radio-mercury.” The activity is completely removed by igniting the mineral. C. H. D.

Cobaltiferous Mispickel from Norway. MARK FLETCHER (*Min. Mag.*, 1904, 14, 54—55).—The axial ratios ($a:b:c=0.6886:1:1.1915$) of some crystals from the Sulitjelma mines in Arctic Norway suggested glaucodote, but the following analysis, by J. A. Smythe, points to a mispickel approaching in composition to the danaite variety.

| S. | As. | Fe. | Co. | Total. | Sp. gr. |
|-------|-------|-------|------|--------|-----------|
| 21.86 | 42.18 | 35.31 | 1.15 | 100.50 | 5.94—6.02 |

L. J. S.

Teallite, a New Sulphostannite from Bolivia; and its Relations to Franckeite and Cyndrite. GEORGE T. PRIOR (*Min. Mag.*, 1904, 14, 21—27).—The new mineral occurs as thin graphite-like folia in association with kaolin, pyrites, wurtzite, and galena. The folia have a greyish-black colour with metallic lustre; their outline is nearly square, and there is a perfect basal cleavage; orthorhombic [$a:b:c=0.93:1:1.31$]. Sp. gr. 6.36; hardness 1—2. The mean (I) of two analyses gives the formula PbSnS_2 .

| | Pb. | Fe. | Zn. | Ag. | Sn. | Sb. | S. | Total. | Sp. gr. |
|------|-------|------|------|------|-------|-------|-------|--------|---------|
| I. | 52.98 | 0.20 | — | — | 30.39 | — | 16.29 | 99.86 | 6.36 |
| II. | 46.23 | 2.69 | 0.57 | 0.97 | 17.05 | 11.56 | 21.12 | 100.19 | 5.88 |
| III. | 48.02 | 2.74 | — | 0.99 | 13.89 | 13.06 | 20.82 | 99.52 | 5.92 |
| IV. | 35.24 | 2.81 | — | 0.50 | 25.65 | 12.31 | 23.83 | 100.34 | 5.46 |
| V. | 34.58 | 2.77 | — | 0.28 | 25.10 | 12.98 | 23.88 | 99.59 | 5.49 |

In physical characters, teallite is very similar to franckeite and cyndrite, each of which has been analysed only once previously. Analyses II and III are of franckeite from Poopó, Bolivia; II being

of material crystallised in square (probably tetragonal) folia, and III of more massive material; formula, $\text{Pb}_5\text{FeSn}_3\text{Sb}_2\text{S}_{14} = 3\text{PbSnS}_2 + \text{Pb}_2\text{FeSb}_2\text{S}_8$. New analyses of cylindrite, also from Poopó, are given under IV and V; formula, $\text{Pb}_3\text{FeSn}_4\text{Sb}_2\text{S}_{14} = 3\text{PbSnS}_2 + \text{SnFeSb}_2\text{S}_8$.
L. J. S.

Bog-iron Ore. D. INGERMAN (*Chem. Centr.*, 1904, ii, 842; from *Pharm. Weekblad.*, 41, 486—488).—The results obtained in estimating the quantity of phosphorus in some samples of bog-iron ore from North Brabant, by dissolving in hydrochloric acid and subsequently precipitating with molybdate, were found to be different from those obtained by heating the substance with sodium carbonate and potassium nitrate and then precipitating with molybdate. It must be assumed therefore that a portion of the phosphorus contained in the ore is combined with iron, possibly in the form of the phosphide Fe_4P_2 .

E. W. W.

Dolomites of Eastern Iowa. NICHOLAS KNIGHT (*Geol. Mag.*, 1904, 493—495).—Analysis, by G. D. Bradshaw, of a dolomite rock used as a building stone gave the following results. The silica is present as quartz-sand, and there is an absence of ferrous oxide.

| CaCO_3 . | MgCO_3 . | SiO_2 . | Al_2O_3 . | Fe_2O_3 . | Total. |
|-------------------|-------------------|------------------|---------------------------|---------------------------|--------|
| 53.62 | 44.96 | 0.83 | 0.25 | 0.34 | 100.00 |

L. J. S.

Triplite and Tourmaline from Östergötland. AXEL HAMBERG (*Geol. Fören. i Stockholm Förhandl.*, 1904, 26, 77—80).—In a large pegmatite-vein traversing gneiss at Skruppetorp, in Godegård parish, there are gigantic crystals of tourmaline, measuring 2—3 metres in length and 3 m. in thickness. Associated with these is dark brown, massive triplite, analysis of which, by Naima Sahlbom, gave the following results. Deducting some water and ferric oxide as being due to the presence of enclosed limonite, this analysis agrees with the usual formula, $\text{R}_2''\text{PO}_4(\text{F}, \text{HO})$. Thin veins in the triplite contain vivianite as an alteration product.

| Al_2O_3 . | Fe_2O_3 . | FeO . | MnO . | CaO . | MgO . | K_2O . | Na_2O . | H_2O . | F . | P_2O_5 . | SiO_2 . | Total, less O for F. |
|---------------------------|---------------------------|----------------|----------------|----------------|----------------|------------------------|-------------------------|------------------------|--------------|--------------------------|------------------|----------------------------|
| 2.16 | 3.40 | 20.48 | 32.60 | 0.80 | 1.33 | 0.33 | 0.98 | 1.25 | 6.96 | 32.33 | 0.11 | 99.80 |

L. J. S.

Occurrence of Thorium in Ceylon. WYNDHAM R. DUNSTAN (*Nature*, 1904, 69, 510).—A black cubic mineral from the gem washings near Balangoda, in the Sabaragamuwa province, was found to contain much more thorium than any previously known mineral, and for it the name *thorianite* is proposed. Analyses by G. S. Blake gave the results under I and II.

| | ThO ₂ . | CeO ₂ . | La ₂ O ₃ . | Di ₂ O ₃ . | ZrO ₂ | UO ₃ . | Fe ₂ O ₃ . | PbO. | SiO ₂ . | Insol. | Total. | Sp. gr. | |
|------|--------------------|--------------------|----------------------------------|----------------------------------|------------------|-------------------|----------------------------------|------|--------------------|--------|--------|---------|------|
| I. | 76.22 | 8.04 | | | trace | 12.33 | 0.35 | 2.87 | 0.12 | — | 99.93 | 9.32 | |
| II. | 72.24 | 6.39 | 0.51 | | | 3.68 | 11.19 | 1.92 | 2.25 | 1.34 | 0.41 | 99.93 | 8.98 |
| III. | 66.26 | 7.18 | — | | | 2.23 | 0.46 | 1.71 | — | 14.10 | — | 99.89* | 4.98 |

* Also: CaO, 0.35; P₂O₅, 1.20; H₂O, 6.40.

Associated with the thorianite is a pale brown mineral, which on a fresh fracture is purplish-brown with a resinous lustre; this is shown by analysis III to be thorite.

Sir WILLIAM RAMSAY (*ibid.*, 69, 533, 559).—The new mineral contains helium (9.5 c.c. per gram.), and a trace only of radium. The high atomic weight (about 240) of the elements precipitated as oxalates and soluble in excess of ammonium oxalate suggests other elements allied to thorium, to the presence of which the high radio-activity is no doubt due.

L. J. S.

[Ceylonese Minerals.] ANANDA K. COOMARA-SWAMY (*Spolia Zeylanica*, 1904, 2, 57—64).—Particulars of the mode of occurrence and localities of thorianite (compare preceding abstract) are given. Notes are added respecting various other Ceylonese minerals, of which the following have been analysed. I, phlogopite from Ampitiya, near Kandy; almost colourless, six-sided crystals, not exceeding four inches across. II, moonstone from Gangapitiya, Central Province; clear and colourless, and free from inclusions. III, kaolin from Alutwela, Central Province; a yellowish-pink clay.

| | SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | MgO. | K ₂ O. | Na ₂ O. | H ₂ O (combined). | Moisture. | Total. |
|------|--------------------|----------------------------------|----------------------------------|-------|-------------------|--------------------|------------------------------|-----------|--------|
| I. | 39.39 | 17.88 | 0.21 | 25.86 | 9.90 | 1.09 | 3.62 | 0.82 | 98.79 |
| II. | 65.70 | 19.85 | 0.17 | — | 8.04 | 5.20 | 0.28 | 0.10 | 99.34 |
| III. | 43.56 | 34.77 | 3.40 | — | 0.28 | 0.36 | 11.90 | 5.63 | 99.90 |

L. J. S.

Pseudo-cubic Antigorite from Sweden. AXEL HAMBERG (*Geol. Fören. i Stockholm Förhandl.*, 1904, 26, 67—76).—Associated with magnetite, chlorite, and calcite at Persberg are irregularly shaped masses of a greenish-white mineral with the composition of serpentine (H₄Mg₃Si₂O₉; anal. I, by Elsa Cronqvist), which is remarkable in possessing perfect cleavages, with pearly lustre, in three directions at right angles to each other. Through all three cleavages are seen biaxial optic figures, negative in sign. The same mineral also occurs in the Ko mine at Nordmarken (anal. II).

| | SiO ₂ . | Al ₂ O ₃ . | MgO. | FeO. | MnO. | Alkalis. | H ₂ O. | F. | Total. |
|-----|--------------------|----------------------------------|-------|------|-------|----------|-------------------|------|--------|
| I. | 43.68 | 0.34 | 38.94 | 4.18 | trace | trace | 12.03 | — | 99.17 |
| II. | 42.90 | 0.51 | 39.19 | 3.90 | trace | trace | 12.30 | 0.97 | 99.77 |

The mineral is very similar to that first described by J. D. Dana (1874) from the Tilly Foster mine, New York, which has been considered to be a pseudomorph of serpentine after periclase. The Swedish mineral is, however, explained as a pseudo-cubic aggregate of antigorite lamellæ.

L. J. S.

[Nephrite from Brazil.] EUGEN HUSSAK (*Ann. naturhist. Hofmus. Wien*, 1904, 19, 85—95).—Worked articles of nephrite accompanied by rough material have been recently found in excavations of ancient Indian tumuli near Baytinga, in southern Bahia. The material varies in colour from dark green to white, and in structure from granular to finely fibrous. Analyses I and II are of pale green and of white material respectively. Microscopical examination shows that there is a passage from the granular material to that with a fibrous structure, and that the latter is in turn altered to a steatitic mineral: the view is expressed that nephrite is a fibrous hornblende of secondary origin.

| | SiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | CaO. | MgO. | P ₂ O ₅ . | H ₂ O. | Total. |
|-----|--------------------|----------------------------------|----------------------------------|------|-------|-------|---------------------------------|-------------------|--------|
| I. | 54·76 | 4·08 | — | 1·80 | 14·31 | 21·26 | 0·40 | 3·72 | 100·33 |
| II. | 57·51 | 3·11 | trace | — | 14·65 | 21·80 | — | 3·39 | 100·46 |

The paper also gives a description of the meteoric stone which fell in 1903 near Uberaba, in Minas Geraes, and of the mineral hamlinite from the diamantiferous sands of Diamantina

L. J. S.

Physiological Chemistry.

Diminution of Carbon Dioxide in the Pulmonary Alveoli of Man on returning from Rarefied Air to the Normal Barometric Pressure. A. AGGAZZOTTI (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 208—215).—The author finds that the volume of air breathed by a man returning from the rarefied air on a mountain (Monte Rosa) to the plain is less than the normal amount, and further, that a less quantity of carbon dioxide is expired, since analysis of the air in the pulmonary alveoli shows an abnormally small proportion of carbon dioxide, although the ventilation of the lungs is less intense.

T. H. P.

Influence of the Barometric Pressure on the Partial Pressures of the Carbon Dioxide and Oxygen in the Pulmonary Alveoli. A. AGGAZZOTTI (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 224—232).—The experiments described show that diminution of the barometric pressure causes an increase in the proportion of carbon dioxide present in the air of the pulmonary alveoli. This increase does not depend on lessening of the ventilation, since barometric depression causes the pulmonary ventilation to become greater than the normal. The partial pressure of the carbon dioxide of the reserve air during the rarefaction is always less than the normal, even when its respiration is greatest; it presents oscillations depending on the quantity of carbon dioxide respired in the different degrees of rarefaction. The partial pressure of the oxygen gradually diminishes as the

rarefaction of the air proceeds, but the diminution is most rapid between 650 mm. and 450 mm., because within these limits the greatest consumption of oxygen takes place as a result of the barometric depression.

T. H. P.

Influence of Inanition and Removal of Blood on the Composition of Blood-plasma. THOS. ST. GITHENS (*Beitr. chem. Physiol. Path.*, 1904, 5, 515—523).—In inanition, the globulin fractions of the blood proteids increase. Removal of blood causes a lessening of the fibrinogen and an increase in the albumin; the figures relating to the serum globulins are inconstant. Probably fibrinogen and albumin have different origins; the globulins do not appear to originate from the albumin. The number of experiments recorded is small.

W. D. H.

Proteolytic Ferment in Leucæmic Blood. O. SCHUMM (*Beitr. chem. Physiol. Path.*, 1904, 5, 583).—The products of the action of this ferment are albumoses, peptone, leucine, tyrosine, lysine, ammonia, and tryptophan.

W. D. H.

Blood Coagulation. LEO LOEB (*Beitr. chem. Physiol. Path.*, 1904, 5, 534—557. Compare *Abstr.*, 1904, ii, 496).—Experiments on the favouring action which tissue extracts have on the coagulation of blood; these were mainly conducted with fluoride plasma and peptone plasma. The question as to how these substances (coagulins) act is discussed.

W. D. H.

Leucocytes and Blood Clotting. FRIEDRICH KRÜGER (*Chem. Centr.*, 1904, ii, 664; from *Arch. exp. Path. Pharm.*, 51, 325—340).—Largely polemical against Ruechel and Spitta, who deny that leucocytes break down during the coagulation of blood. In the blood of cats and dogs it is the polymorpho-nuclear cells which mainly break down.

W. D. H.

Ether-laking. S. PESKIND (*Amer. J. Physiol.*, 1904, 12, 184—206).—The experiments are in favour of the hypothesis that the cause of ether-laking is the solution and extraction of lecithin and cholesterol from the envelopes of the blood-corpuscles. The same percentage of ether brings about laking as is necessary to dissolve lecithin and cholesterol. The weak point of the theory appears to be that ether (or chloroform) which is saturated with cholesterol, laves blood just as though no cholesterol were dissolved in it.

W. D. H.

Influence of Cathions on the Coagulability of the Blood. GIUSEPPE BUGLIA (*Atti R. Accad. Torino*, 1903—1904, 39, 921—956).—Of a large number of salts examined by the author, all except two (mercuric chloride and silver nitrate) are capable of rendering blood non-coagulable. The proportions of the various salts required to effect this change vary very considerably, and the intensity of the anti-coagulating action is closely related to the chemical nature of the metal in the salt; the most active salts in this direction are those of

the heavy metals, less active are those of the alkaline-earth metals, whilst salts of the alkali metals are only very slightly active.

Further, with most, but not all salts, it is possible to restore the coagulability of the blood by various means. The salts are hence divisible into two groups: (1) this comprises salts which only prevent blood from coagulating when in moderately large doses, which produce no profound change in the physical aspect of the blood, and can have their action annulled by the addition of physiological or chemical solutions of serum. (2) In this group are those salts which, in very small doses, prevent the coagulation, which produce in the blood changes visible macroscopically (formation of white floccules), and the action of which is destroyed neither by dilution, nor by precipitants, nor by the addition of serum.

The anti-coagulating power of salts only comes into action for a certain minimum or critical molecular concentration, and when this is exceeded the blood remains persistently liquid.

In determining the anti-coagulating power of a salt, in some cases the cation is very active and the anion only slightly so, whilst in others it is the anion which is the more active. T. H. P.

Fate of Salt Solutions in the Human Stomach. CASIMIR VON RZENTKOWSKI (*Chem. Centr.*, 1904, ii, 719—720; from *Arch. exp. Path. Pharm.*, 51, 289—309).—The experiments were made on a boy sixteen years old on whom, on account of the complete obstruction of the œsophagus, the result of poisoning by alkali, the operation of gastrostomy had been performed. Nutriment was supplied exclusively from the opening in the abdomen. When a hypertonic solution containing 5.85 per cent. of sodium chloride was introduced, it was found that it became strongly diluted in the stomach, so that the work of the intestine was facilitated, but the solution did not become isotonic with the blood. The rapidity with which sodium chloride solutions left the stomach was to a certain extent dependent on the concentration. In the case of pure water, 7 c.c. disappeared in a minute, but a normal solution of sodium chloride required three times as long. Slightly hypotonic solutions of sodium chloride and pure water cause irritation of the stomach and induce secretion, the concentration being thereby increased. This occurs the more rapidly the less the concentration of the sodium chloride solution. The increase of concentration is not caused by the separation of hydrochloric acid, since this acid could not be detected in the contents of the stomach. When hypotonic solutions of solvents such as egg and water, or milk, egg, and water were administered, the contents of the stomach soon became isotonic with the blood owing mainly to the separation of hydrochloric acid. Opium caused the dilution of hypertonic solutions to take place with twice the normal rapidity. E. W. W.

The Proteolytic and Rennet-like Action of Different Digestive Juices. J. P. PAWLOFF and S. W. PARASTSCHUK (*Zeit. physiol. Chem.*, 1904, 42, 415—431).—The two actions of various digestive juices (gastric, pancreatic, intestinal) in producing milk coagulation

and proteolysis run parallel. Pancreatic juice does not clot milk until it is activated. The experiments lend support to the view that the two actions are not due to different ferments.

W. D. H.

Solubility of Milk and Casein in Pepsin-hydrochloric Acid.

ARTHUR ZAITSCHEK and F. VON SZONTAGH (*Pflüger's Archiv*, 1904, 104, 550—563).—Digestion experiments with pepsin-hydrochloric acid show that the milk and casein of woman, ass, and mare are entirely digested; whereas those of the cow, buffalo, and goat are not. The latter kinds of milk yield a larger amount of pseudo-nuclein than the casein prepared from them does. The milks of the first class contain less casein and a relatively smaller part of the total nitrogen in the casein than those of the second. The addition of thymol, toluene, and chloroform hinder digestibility, so also does drying the casein at 110°.

W. D. H.

Artificial Digestion of some Compounds of Casein and Paracasein contained in Cottage and Cheddar Cheese. LUCIUS L. VAN SLYKE and EDWIN B. HART (*Amer. Chem. J.*, 1904, 32, 154—164).—It is popularly believed that fresh cottage or Dutch cheese, which consists essentially of casein dilactate with 70—75 per cent. of moisture, is more easily digested than new Cheddar cheese, in which the nitrogen is present mainly as paracasein monolactate. In order to test this view, experiments have been carried out on the action of pepsin, in presence and absence of hydrochloric acid, on paracasein, paracasein monolactate and dilactate, and casein monolactate, dilactate, and dihydrochloride. The results show that in the absence of acids paracasein is not digested, whilst the other compounds undergo partial digestion, the monolactates of paracasein and casein being digested to a greater extent than the corresponding dilactates. In the presence of 0.4 per cent. of hydrochloric acid, paracasein dilactate is more readily digested than the monolactate; paracasein mono- and di-lactates and casein mono- and di-lactates and dihydrochloride digest more completely in the presence of hydrochloric acid than in its absence. The addition of acid after digestion has commenced causes a larger quantity of proteid to be digested both in cottage and Cheddar cheese. Casein dilactate and dihydrochloride are digested by pepsin at the same rate and to the same extent. Cottage cheese made from whole milk is digested more quickly than that made from skim-milk owing to the looser texture of the former; the fat present does not retard digestion. The digestibility of cottage cheese is greater than that of Cheddar cheese owing to the fact that in presence of hydrochloric acid casein dilactate is more easily digested than paracasein monolactate, and also because cottage cheese, as ordinarily consumed, is in a finer state of division than Cheddar cheese, and is therefore more readily attacked by digestive agents.

E. G.

Feeding Experiments with Hydrolysed Casein. EMIL ABDERHALDEN and PETER RONA (*Zeit. physiol. Chem.*, 1904, 42, 528—539).—The simple cleavage products (polypeptides, &c.) of casein, obtained by the use of pancreatin, pepsin-hydrochloric acid, and acids, were

administered to mice. The animals maintained their weight and health, and the experiments furnish additional proof of the synthesis of the proteids of the body from simple substances. W. D. H.

Digestibility of Chitin and the Nutritive Value of Insects. ARTHUR ZAITSCHEK (*Pflüger's Archiv*, 1904, 104, 612—623).—The experiments were made on birds to the food of which the insect *Palingenia longicauda* was added. It was found that chitin was wholly undigested, but the remainder of the insect forms a source of considerable energy. The experiments were given with full details, energy as usual being reckoned in calories. W. D. H.

How does an Excess of Calcium Carbonate in Food affect the Utilisation of the Food Constituents? JAKOB VOLHARD (*Landw. Versuchs-Stat.*, 1904, 61, 305—312).—The results of experiments in which two sheep were each fed for 18 days with meadow hay (700 grams), cotton-seed meal (200 grams), sodium chloride (10 grams), and calcium carbonate (50 grams) per day, showed that the calcium carbonate had no appreciable effect on the assimilation of the food. The faeces contained more than 6 per cent. of calcium carbonate in the dry matter.

Weiske (*J. Landw.*, 1885, 33, 21) showed that addition of sulphuric acid to hay ($\text{SO}_3 = 7.5$ grams per kilo.) did not interfere with the digestion of sheep. N. H. J. M.

Effect of Food Fat and some other Food Constituents on the Production of Milk. AUGUST MORGEN, CARL BEGER, GUSTAV FINGERLING, PAUL DOLL, ERWIN HANCKE, HERMAN SIEGLIN, and WILLY ZIELSTORFF (*Landw. Versuchs-Stat.*, 1904, 61, 1—284. Compare Abstr., 1902, ii, 107).—The experiments were made with sheep (1900—1903) and with goats (1901—1903).

Food almost free from fat maintained the animals in a healthy condition and increased the live weight, but it is unsuitable to milk production. Addition of digestible proteids in the place of corresponding amounts of carbohydrates was favourable to milk production, but was without effect on the percentage of fat in the dry matter. Food fat (0.5—1 gram per kilogram of live weight) promotes the production of milk fat; a larger amount of food fat is sometimes favourable and sometimes unfavourable, but generally is without further effect.

Addition of oil to food raises the iodine and refractometer numbers of the milk fat, but no other changes in the nature of the milk fat were observed; and earth nut oil and mutton tallow gave almost identical results.

Whilst food fat is especially suitable for the production of milk fat, it is only of secondary importance as a maintenance food. Carbohydrates cannot take the place of food fat. The employment of stimulants is only desirable in special cases. N. H. J. M.

The Tissues as Water-reservoirs. W. ENGELS (*Chem. Centr.*, 1904, ii, 665; from *Arch. exp. Path. Pharm.*, 51, 346—360).—Dogs were allowed to fast for 4 days, and their tissues were then freed from blood; the amount of water in the animals comprised 66 per cent. of their

weight. 42·8 of the body consists of muscles, and contains 47·7 per cent. of the water of the body; 16·1 consists of skin containing 11·6 per cent. of the water; the rest of the body (41 per cent.) contains the rest of the water (40·7 per cent.). By injection of 0·6 per cent. solution of sodium chloride intravenously, the muscles and skin take up most water; the muscles take up 67·9 per cent. of the water added to the body, and are therefore the most important from the point of view of water-reservoirs.

W. D. H.

Amount of Calcium in Various Animal Organs. M. TOYONAGA (*Bul. Coll. Agr. Tōkyō*, 1904, 6, 89—95).—Smooth and striped muscles (horse) contained respectively 0·050 and 0·046 calcium per thousand, the relations Ca:Mg being 0·24:1 and 0·29:1. The amount of calcium in the testicles of horses and bulls is less than in the pancreas, spleen, and liver, whilst the relation Ca:Mg is higher.

Determinations of calcium and magnesium were also made in the brains of calves and horses, and in the milk glands of cows. The results are summarised, together with those obtained by other investigators with various animal organs.

N. H. J. M.

Taurine in Molluscan Muscle. LAFAYETTE B. MENDEL (*Beitr. chem. Physiol. Path.*, 1904, 5, 582).—Taurine was separated from extracts of muscle and from the hepato-pancreas of various marine gasteropods.

W. D. H.

Nucleo-proteid of the Liver. II. JULIUS WOHLGEMUTH (*Zeit. physiol. Chem.*, 1904, 42, 519—523. Compare Abstr., 1903, ii, 440).—One hundred grams of nucleic acid from the nucleo-proteid of the liver yield 2·25 grams of xanthine, 2·54 of guanine, 1·9 of adenine, and 1·79 grams of hypoxanthine. In contrast with thymus-nucleic acid, the yield of guanine and xanthine is greater and of adenine less; the amount of hypoxanthine is about equal in the two cases.

W. D. H.

Ferments and Fatty Degeneration. RICHARD WALDVOGEL (*Zeit. physiol. Chem.*, 1904, 42, 200—206).—During aseptic autolysis of the liver, the amounts of jecorin, protagon, fatty acids, cholesterol, and neutral fats increase; that of lecithin diminishes. Very similar results are obtained in livers of dogs poisoned with phosphorus, or by the addition of sterile liver extracts to lecithin. The change is attributed to ferment action, and is believed to be similar during autolysis and during fatty degeneration.

W. D. H.

Absorption of Uric Acid and Sodium Urate. J. J. VAN LOGHEM (*Ann. Inst. Pasteur*, 1904, 18, 468—480).—Freudweiler (*Deut. Archiv. Klin. Med.*, 1899, 63, 266) states that uric acid crystals introduced under the skin of rabbits disappear by phagocytic action. This is not the case; they dissolve readily both *in vivo* and *in vitro* in the tissue juices. From such juices it is easy to obtain a precipitate of sodium urate like gouty tophi; this does not occur in normal

tissues. If sodium urate is precipitated in the tissues or introduced there by injection, it disappears by phagocytic action, the phagocytes secreting in their protoplasm an acid which dissolves it. The bearing of these observations on theories of gout is discussed. W. D. H.

Uric Acid Formation in Tissue Extracts. ALFRED SCHITTENHELM (*Zeit. physiol. Chem.*, 1904, 42, 251—258).—Horbaczewski was the first to show the formation of uric acid from nuclein in spleen pulp. Adenine and guanine pass into uric acid almost quantitatively. The present paper gives experiments to show that the addition of sodium α -nucleinate to extracts of spleen, liver, and lung leads at 40—45° in three days (air being passed through the mixture and chloroform added as antiseptic) to the formation of uric acid; the amount found accounts for about two-thirds of the purine compounds originally present. The change is attributed to ferment action; the ferment is precipitable by ammonium sulphate, and is inhibited by alcohol. W. D. H.

Composition of Buffalo Milk. RICHARD WINDISCH (*Zeit. Nahr. Genussm.*, 1904, 8, 273—278).—The results of the analyses of samples of milk obtained from three buffalo cows are given. Both the morning and evening milk were analysed, about 42 samples in all being examined. The averages of the results were as follows:

| | Morning milk. | Evening milk. |
|---------------------|-----------------|-----------------|
| Total solids | 20.12 per cent. | 18.83 per cent. |
| Fat | 9.20 " | 7.87 " |
| Ash | 0.775 " | 0.831 " |
| Sp. gr. of milk ... | 1.0310 | 1.0326 |
| " serum ... | 1.0319 | 1.0325 |

W. P. S.

Fate of Strychnine in the Rabbit's Intestine. ROBERT A. HATCHER (*Amer. J. Physiol.*, 1904, 12, 237—240).—The contents of the rabbit's cæcum and colon do not completely destroy strychnine under the conditions of the experiments described. It is doubtful whether any real destruction occurs under any conditions, in spite of Salant's statements to the contrary. W. D. H.

Freezing Point and Conductivity of Urine in Pharmacological Experiments. HEINRICH DRESER (*Zeit. Elektrochem.*, 1904, 10, 656—661).—The blood and other fluids in the bodies of warm-blooded animals have a freezing point which never differs much from -0.56° . Hence, in cases of dropsy the elimination of salt is as essential as that of water, since each gram of salt retains some 100 grams of water in the system. The author has found determinations of the freezing point and of the conductivity of the urine in such cases to be a very useful means of determining the total quantity of dissolved substance and of electrolytes in it. Among the usual diuretics, theocin produces a largely increased excretion of electrolytes, and is therefore capable

of producing a permanent reduction in the quantities of water retained in the body, whilst the other diuretics only produce an increased elimination of water, which is reabsorbed at the first opportunity.

T. E.

Calorimetry of Urine. KOLOMAN FARKAS and MICHAEL KORBULY (*Pflüger's Archiv*, 1904, 104, 564—607).—Aqueous solutions of urea undergo a loss of energy by drying, but this is least when the drying is carried out in a vacuum at the ordinary temperature. The presence of hydrochloric acid does not hinder the loss of energy or of nitrogen. The loss of energy and of nitrogen are not parallel, and the proportion of the two is irregular. The same loss is noticeable on drying urine, especially at high temperatures and if the urine is alkaline. The use of Kellner's cellulose blocks is not recommended. Such facts show that the data given by Rubner and Krummacker in their investigations on metabolism need correction.

W. D. H.

Urine of Herbivora. ERNST SALKOWSKI (*Zeit. physiol. Chem.*, 1904, 42, 213—250).—The principal points to which attention is drawn are: (1) The occurrence of allantoin as a frequent normal constituent of cow's urine; this substance crystallises out with calcium hippurate on evaporating the urine. The relation of allantoin to oxalic acid in metabolism is discussed. (2) The large amount of sulphuric acid in horse's urine which is excreted in combination with glycuronic acid. (3) The large amount of indican in the same urine, its origin in the body, and the methods for estimating it.

W. D. H.

Production of Sugar in the Kidney of the Dog under the Influence of Phloridzin. RAPHAEL LÉPINE and BOULUD (*Compt. rend.*, 1904, 139, 497—499).—The observation that blood from the renal vein often contains more sugar than arterial blood is confirmed. Asphyxiation results in a considerable increase of sugar in the arterial blood, but not in the blood from the renal vein. From this it is deduced, that oxygen is necessary for the production of sugar from some other carbohydrate (*sucre virtuel*) (compare this vol., ii, 56). Both primary (immediate) and secondary (produced in one hour *in vitro*) sugars may be present in renal blood in excess of that in arterial blood.

H. M. D.

Amino-acids in Urine. EMIL ABDERHALDEN and LEWELLYS F. BARKER (*Zeit. physiol. Chem.*, 1904, 42, 524—527).—If the naphthalene- β -sulphonic reaction is combined with Fischer's esterification method, amino-acids can be detected and separated in urine. The poisoning of dogs with phosphorus, glycine, leucine, and phenylalanine were thus detected.

W. D. H.

Excretion of Uric Acid, administered in Various Ways to Rabbits. ERNST BENDIX and ALFRED SCHITTENHEIM (*Zeit. physiol. Chem.*, 1904, 42, 461—463).—After intravenous injection of uric acid (dissolved in piperazine solution), a large amount appears in the urine;

after administration by the mouth, only traces ; after subcutaneous injection, an intermediate result is obtained. W. D. H.

Parent Substance of the Hippuric Acid produced in the Organism of Herbivorous Animals. THEODOR PFEIFFER, R. RIECKE, and C. BLOCH (*Bied. Centr.*, 1904, 33, 620—625 ; from *Mitt. landw. Inst. Univ. Breslau*, 2, Heft. 4).—The addition of readily digestible carbohydrates to a food which produces much hippuric acid causes a slight reduction in the amount formed, whilst an exclusive increase of digestible proteids slightly increases the amount of hippuric acid. Increasing the alkalinity of the urine by adding sodium acetate to the food has no effect.

As compared with gramineous hay, clover-hay contains only small amounts of the parent substance of hippuric acid. The substance present in meadow-hay is to a great extent soluble in hot water. Cherry-gum and coniferin produce hippuric acid, whilst pure arabinose does not. Crude fibre contains the parent substance, but in very varying amounts according to its origin. In the case of clover-hay, most of the hippuric acid is derived from the digestible crude fibre, whilst in the case of meadow-hay the crude fibre is relatively unimportant in this respect. N. H. J. M.

Origin and Precursors of Urinary Indican. FRANK P. UNDERHILL (*Amer. J. Physiol.*, 1904, 12, 176—183).—The quality as well as quantity of the nitrogenous constituents of food influences indican excretion. Gelatin causes a diminution of putrefactive products and reduces in dogs the amount of urinary indican. This may be of therapeutic value. W. D. H.

Urinary Proteid. KARL A. H. MÖRNER (*Beitr. chem. Physiol. Path.*, 1904, 5, 524—533).—Polemical against Oswald (this vol., ii., 358), who holds that the small amount of proteid in normal urine is a globulin. W. D. H.

The Resorcinol Reaction in Urine. RUDOLF ADLER and OSCAR ADLER (*Zeit. physiol. Chem.*, 1904, 42, 567).—Polemical against Rosin (this vol., ii, 595). W. D. H.

Ureine. H. D. HASKINS (*Amer. J. Physiol.*, 1904, 12, 162—166).—Moor's ureine is a mixture of several substances. It contains a large admixture of urochrome. The reactions which Moor believes establish the existence of ureine are in reality the characteristic reactions of urochrome. W. D. H.

New Toxin of the Urine. FRANCESCO MARINO-ZUCO (*Gazzetta*, 1904, 34, ii, 97—101).—By evaporating healthy human urine under rigorously aseptic conditions, the author has obtained a new toxin, which, when purified by precipitation with 90 per cent. alcohol and dialysis of its aqueous solution, is precipitated from the latter by a small quantity of sodium chloride as a white, amorphous powder insoluble in alcohol and perfectly odourless. The amount obtained is from

0.3 to 0.5 gram per litre of urine. It is unchanged in dry air, but in presence of moisture rapidly assumes a brown colour. Its activity diminishes gradually and is best maintained in the dark and in a perfectly dry atmosphere. When heated with sodium carbonate and potassium nitrate, it gives a residue yielding a precipitate with ammonium molybdate solution. It gives Liebermann's proteid reaction and the xantho-proteid reaction.

When injected into animals, it produces an almost immediate change of the temperature, which may rise to 41° and fall to below 30°. With large doses, death ensues in twelve hours; with very small doses, marked changes in temperature always supervene and the animals resist it for a month or more, but finally succumb in a comatose condition. Autopsy reveals a characteristic gelatinous oedema filtering in at the point of inoculation, and the medullary portion of the sub-renal capsule is either completely apoplectic, as in acute poisoning, or considerably congested, as in slow poisoning. This behaviour indicates that the toxin possesses enzymic properties.

T. H. P.

Composition of Fæces during Different Diets. N. P. SCHIERBECK (*Arch. Hygiene*, 1904, 51, 62—95).—A very exhaustive examination of human fæces during different diets. In agreement with earlier researches by Prausnitz, it is found that the total nitrogen, ash, and ethereal extract have a constant relation to the total dry residue of the fæces in the same individual on an ordinary mixed diet. The same holds good for proteid nitrogen, cellulose, and pentosans. The amounts are independent of the amounts of these materials in the diet. The total nitrogen of the fæces is not, however, constant in different individuals on a mixed diet, and in some cases is higher on a diet of rye bread than in one which is presumably more completely absorbed. Attention is drawn to individual differences, and the cause of such is discussed.

W. D. H.

The Action of Purgatives and their Inhibition by Calcium Salts. JOHN B. MACCALLUM (*Pflüger's Archiv*, 1904, 104, 421—432).—Experiments on rabbits and dogs were made with saline purgatives, cascara and rhubarb, and pilocarpine, all administered subcutaneously. Saline purgatives increase peristalsis and intestinal secretion; both are inhibited by calcium chloride and magnesium chloride. The action is independent of the connection of the intestine with the central nervous system. The same is true for the vegetable purgatives cascara and rhubarb. In the case of pilocarpine, the antagonism of calcium chloride is not so marked.

W. D. H.

Inorganic Constituents of Tumours. S. P. BEEBE (*Amer. J. Physiol.*, 1904, 12, 167—172).—Analyses, mainly of the ash, in eight malignant and one benign tumour are given. Sulphur, phosphorus, nitrogen, iron, calcium, sodium, and potassium were determined. The results in some cases are very uniform, but the experiments are at present too few to enable definite conclusions to be drawn.

W. D. H.

Effects of Certain Stimuli on Paramœcium. ELIZABETH W. TOWLE (*Amer. J. Physiol.*, 1904, 12, 220—236).—*Paramœcium* lives in pure water; it becomes readily habituated to solutions of various substances which are not rapidly fatal. Low temperatures cause loss of water and condensation of protoplasm; various chemical solutions containing predominant cations act similarly, but secondary effects leading to swelling and liquefaction may follow. The actions of a number of substances are described, and also a certain amount of antagonism between different agents. W. D. H.

Importance of Sodium in the Functions of the Spinal Medulla. SILVESTRO BAGLIONI (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 194—201).—On placing the isolated spinal medulla and the sciatic nerve of a frog in isotonic solutions of indifferent chemical substances (dextrose, sucrose, mannitol, glycerol, and asparagine) containing no trace of sodium salts, the reflex excitability of the centres and then the direct excitability of the peripheral nerve disappear in from 2 to 4 hours. If, however, these solutions contain in addition a small proportion of a sodium salt (0·2 per cent. of sodium chloride), the excitability persists. If the spinal medulla and the nerve, rendered inexcitable in the above manner, are placed for a short time ($\frac{1}{2}$ or $\frac{3}{4}$ hour) in the solution containing a sodium salt, they again acquire their full excitability; sodium chloride is the most active in this respect, then follow the hydrogen carbonate and nitrate. This revival is not produced by salts of metals allied to sodium, for instance, chloride of potassium or lithium. T. H. P.

Chloroform Anæsthesia. VICTOR HORSLEY and others (*British Med. J.*, 1904, ii, 720—729).—This is an account of an important discussion held at the recent meeting of the British Medical Association. Those who participated were the majority of British physiologists who have investigated the scientific bearings of the subject, and also the leading anæsthetists of the country. The principal practical point on which all agreed was that 2 per cent. of chloroform vapour in the air was all that is necessary, and beyond this danger lies. Speakers differed as to the form of apparatus by which this may be accomplished, those of Vernon Harcourt and of Dubois being more especially considered. W. D. H.

Influence of Chloroform on Intravital Staining with Methylene-blue. CHRISTIAN A. HERTER and A. N. RICHARDS (*Amer. J. Physiol.*, 1904, 12, 207—212).—Although the results found in rabbits were not uniform, there is evidence of diminished reduction on the part of chloroformed brains. The increased circulation of the dye in the blood is due to the impaired excretory activity of kidneys and liver. This explains a more abundant passage of the dye into the digestive tract, and the tint of the blood in part accounts for the appearance of the brain. The muscles, however, are less deeply stained than in the control animals. Ether acts similarly, except that the heart is less stained than in chloroformed animals, and less of the dye passes into the alimentary tract. W. D. H.

Employment of Reducible Pigments in the Study of Poisons. CHRISTIAN A. HERTER (*Zeit. physiol. Chem.*, 1904, 42, 493—501).—The experiments were made on animals under the influence of various poisons, so as to test under these conditions the reducing action of the tissues on methylene-blue. The effect of narcosis is described in the preceding abstract. The results with hydrocyanic acid were variable, but the central nervous system is more deeply injured than other parts of the body. In poisoning by coal gas, many of the voluntary muscles are deeply pigmented with the methylene-blue; the same is true for the liver to a slight extent. It requires an almost fatal lessening of the oxygen of the blood to affect the reducing action of most tissues. A low body temperature lessens the action. In adrenaline poisoning, the kidneys are usually pale and secrete but little urine; the brain is bluer than in normal animals, and the suprarenals are deeply pigmented when the kidneys are inactive. W. D. H.

Physiological Action of Alcohol at Great Altitudes. ANGELO MOSSO and GINO GALEOTTI (*Atti Real. Accad. Lincei*, 1904, [v], 13, ii, 3—12).—From experiments made on Galeotti, it is found that in the plains (in Turin) the ingestion of alcohol effects considerable changes in the organism, causing the temperature to rise, the respiration to become accelerated, and the proportion of carbon dioxide in the expired air to increase; on the summit of Monte Rosa, however, alcohol produces no change in the temperature or respiration, the only effect being that the carbon dioxide in the breath is augmented. It appears, then, that the sensitiveness of the nervous cells to the action of alcohol is diminished at great altitudes. T. H. P.

Physiological Action of Carbocyclic Acids. ERNST PRIBRAM (*Chem. Centr.*, 1904, ii, 668; from *Arch. exp. Path. Pharm.*, 51, 372—382).—The sodium salts of the following acids given in various ways act as diuretics: benzoic, toluic, *p*-hydroxybenzoic, cinnamic, mandelic, protocatechuic, benzoylacetic, phthalic, gallic, hippuric, and camphoric. Some increase the urinary nitrogen; others do not. Phthalic acid is excreted quantitatively in the rabbit. W. D. H.

Alkyl Synthesis after Administration of Thiourea. JULIUS POHL (*Chem. Centr.*, 1904, ii, 668; from *Arch. exper. Path. Pharm.*, 51, 341—345).—If thiourea is given to dogs, cats, or rabbits by the mouth, under the skin, or by intravenous injection, the expired air contains an alkyl sulphide, probably ethyl sulphide (3 to 4 mg. in the 24 hours); the urine also contains abnormal odorous substances. Alkyl sulphide is also found in the muscles, and its occurrence is not prevented by extirpation of the kidneys. Ammonium thiocyanate, sodium sulphite, and sulphocarbaniide produce no such effect, but dimethylthiourea and thiosinamine do. W. D. H.

Fate of Potassium Myronate in the Animal Organism and its Hydrolysis by the Ferments of the Liver. JOSEPH H. KASTLE and ELOISE CHESLEY MCCAW (*Amer. Chem. J.*, 1904, 32, 372—376).—When potassium myronate is injected subcutaneously into animals, it passes unchanged into the urine and is not directly assimilable from the blood. If, however, the salt is administered by the mouth, it undergoes assimilation, probably through the agency of the liver. The action of aqueous extracts of the livers of various animals on potassium myronate has been investigated, and it is found that in all cases, except that of the fish, the liver contains a ferment capable of effecting the hydrolysis of the glucoside. The results seem to indicate that the hydrolysis of potassium myronate by animal myrosin takes place in two stages, in the first of which dextrose is liberated, whilst in the second the residue undergoes decomposition into allylthiocarbimide and potassium hydrogen sulphate. E. G.

Action of Muscarine and Pilocarpine on the Heart. H. MACLEAN (*Brit. Med. J.*, 1904, ii, 740).—There is an exact correspondence between the effects of electrical excitation of the inhibitory mechanism of the heart and those of muscarine and pilocarpine poisoning. These alkaloids act not on muscle directly, but on the inhibitory mechanism, and on the terminal parts of that mechanism not on ganglion cells. W. D. H.

Inhibition of the Action of Physostigmine by Calcium Chloride. SAMUEL H. MATTHEWS and ORVILLE H. BROWN (*Amer. J. Physiol.*, 1904, 12, 173—175).—The action of physostigmine in producing contractions of the intestine and tremors of voluntary muscles is counteracted by calcium chloride. The increased salivary secretion is partly counteracted. The experiments were made on dogs. W. D. H.

Hydrogen Cyanide and its Toxicological Detection. DOMENICO GANASSINI (*Chem. Centr.*, 1904, ii, 718—719; from *Boll. soc. med.-chir., Pavia.*).—Experiments on rabbits have shown that hydrogen cyanide is not a hæmatic poison in the strict sense of the term. It combines with the methæmoglobin of the blood, and in some cases, in which a large amount has been administered, the blood shows the reactions of cyanohæmoglobin after a few days, but, as a rule, hydrogen cyanide is not present in the blood, or at most in traces. Even when large quantities of the poison are taken, it cannot be detected in the brain, and when administered subcutaneously, or by the mucous membrane, neither the various fluids of the body nor the organs or tissues show the slightest trace of the acid except at the place where it was introduced into the organism. With the same rapidity with which it attacks the cells, especially those of the nervous system, it is converted into other substances, which are quickly eliminated, and for this reason a quantity merely necessary to cause death cannot be detected, but only the excess, which remains unchanged for a comparatively long time. In connection with Robert's colour tests with potassium ferricyanide and potassium chlorate, the following reactions are cited. When a few drops of a

1 per cent alcoholic solution of guaiacum resin tincture are allowed to fall into blood which contains hydrogen cyanide, to which a few drops of a dilute solution of copper sulphate have been added, a more or less intense blue coloration is formed at the surface. By treating diluted blood with a grain of potassium percarbonate, a yellowish-green coloration is immediately formed if hydrogen cyanide is present. A preliminary test with Schönbein's paper rendered more sensitive by Brünnich's method has little practical value. The most suitable method of removing the hydrogen cyanide from the material to be examined is, in most cases, to distil after strongly acidifying with tartaric acid. Jacquemin's method of separating cyanides from ferro- and ferri-cyanides is not free from difficulties. Hydrogen cyanide is best detected in the distillate by means of the Prussian blue reaction, preferably by Vitali's method. Schauenstein's assumption that hydrogen cyanide is wholly or partly converted into ammonium formate in the organism can scarcely hold; the formation of uro-xanthine compounds, xanthine, or monomethylxanthine is more probable.

E. W. W.

Chemistry of Vegetable Physiology and Agriculture.

Chemical Changes in the Souring of Milk. LUCIUS L. VAN SLYKE and EDWIN B. HART (*Amer. Chem. J.*, 1904, 32, 145—154).—When milk turns sour, lactic acid is produced by fermentation of the lactose and the milk-casein becomes coagulated. Various explanations of the action which produces the coagulation have been proposed, but its nature has not yet been satisfactorily established.

Experiments have been carried out with the object of ascertaining the quantities of casein monolactate and dilactate formed in the souring of milk and the conditions under which lactose is converted into lactic acid. It has been found that at 18—27° the decomposition of the lactose takes place rapidly for 32 hours, then gradually diminishes, and ceases in 72—96 hours. The maximum loss of lactose amounts to 1·5 per cent., or about 28 per cent. of the sugar originally present in the milk; the lactic acid produced is about 0·9 per cent., which is equivalent to 62 per cent. of the lactose decomposed. The coagulation of the milk at 18—27° occurs in 24—29½ hours, the total acid present at this point being 0·6—0·7 per cent. When the coagulation of the milk is first apparent, 13—14 per cent. of the casein is in the form of monolactate and 86—87 per cent. in the form of dilactate, but as the quantity of acid increases, the monolactate is converted into the dilactate.

E. G.

Mannitic Fermentation. ULISSE GAYON and ELISÉE DUBOURG (*Ann. Inst. Pasteur*, 1904, 18, 385—386).—Mazé and Perrier have studied the production of mannitol by a microbe obtained from wine, and by means of a ferment previously isolated by the authors. They find neither glycerol nor succinic acid as products, and, further, they find alcohol in fermentations of levulose and haricot broth. This is what the authors did not find; they have in consequence repeated

their experiments under the conditions employed by Mazé and Perrier, but confirm their previous conclusions. W. D. H.

Dysentery Toxin and Antitoxin. CHARLES TODD (*J. Hygiene*, 1904, 4, 480—494).—Old cultures of *Bacillus dysenteriae* (Kruse) in alkaline broth contain a soluble toxin. This is also contained in the bodies of the young bacilli. The horse and rabbit are susceptible, the guinea-pig, rat, and mouse resistant, to this toxin. Immunisation may be produced in the horse, and the antitoxic power of horse-serum so obtained reaches a high value; this may be used for preventive inoculation. The toxin and antitoxin neutralise each other *in vitro*, provided sufficient time is allowed. Shiga's dysentery bacillus, and the bacillus of asylum dysentery in England, yield a similar toxin, which can be neutralised by the antitoxin prepared by means of Kruse's bacillus. Flexner's bacillus, and that of summer diarrhoea obtained from America, do not yield a soluble toxin. W. D. H.

Biochemistry of the Sorbose Bacterium. GABRIEL BERTRAND (*Ann. Chim. Phys.*, 1904, [viii], 3, 181—288).—A *résumé* of work already published (compare Abstr., 1896, ii, 494; 1898, i, 550, 556; ii, 397; 1899, ii, 44, 170; 1900, i, 377; 1902, ii, 159; Maquenne and Bertrand, Abstr., 1901, i, 497; and Sazerac, Abstr., 1903, ii, 606). M. A. W.

Some Constituents of Yeast. OSCAR HINSBERG and ERNST ROOS (*Zeit. physiol. Chem.*, 1904, 42, 189—192. Compare Abstr., 1903, ii, 565).—If an alcoholic extract of yeast is freed from alcohol and shaken with ether and excess of dilute sodium carbonate solution, the upper ethereal layer contains yeast fat, cholesterol, and the ethereal oil of lecithin; the lower layer contains peptonoids, xanthine bases, and small quantities of fatty acids. If dilute sodium hydroxide is used instead, the lower layer contains phosphorised materials, the result of lecithin decomposition; the ethereal layer is almost free from lecithin, and contains yeast fat, yeast oil, and cholesterol; the last traces of lecithin can be removed by again shaking with 1 per cent. sodium hydroxide solution. The melting points of the fatty acids obtained from the yeast fat were investigated; palmitic acid was identified, and another acid with higher melting point, but whether this is stearic acid or not is uncertain. W. D. H.

Respiration Coefficient of the Unicellular Alga, Chlorothecium Saccharophilum. LUDMILA PETRASCHESKY (*Chem. Centr.*, 1904, ii, 663—664; from *Ber. deut. bot. Ges.*, 22, 323—327).—Palladin showed that this alga is a typical aërobe, and its respiratory coefficient (CO_2/O_2) is less than unity. If brought into an atmosphere of hydrogen, it excretes carbon dioxide, but this soon ceases; it, however, recovers the property when air is once more admitted. In an atmosphere free from oxygen it decomposes complex compounds into simpler ones. A connection between respiratory and fermentative processes is suggested. In the present paper, it is shown that in raffinose the coefficient is greater than unity, and in mannitol smaller than normal; the explanation is that, by intramolecular respiration

in an atmosphere free from oxygen, acids are formed in the former medium and alcohol-like substances in the latter. W. D. H.

Assimilation of Atmospheric Nitrogen by a Fungus found in Peat. CHARLOTTE TERNETZ (*Chem. Centr.*, 1904, ii, 461; from *Ber. deut. bot. Ges.*, 22, 267—274).—A fungus, "oxycoccus," which has the power of assimilating atmospheric nitrogen, has been found in peat and peaty soil, and has been isolated from the roots of various indigenous *Ericaceæ*. The fungus has a branched mycelium with septa, and forms brown pycnidia, which contain very small hyaline spores. The assimilation of nitrogen takes place under aërobic conditions of life, and does not cause fermentation of dextrose. The action of the fungus is not as rapid as that of *Clostridium Pastorianum*, but involves less waste. E. W. W.

Processes of Assimilation. HANS EULER (*Ber.*, 1904, 37, 3411—3418).—The author confirms Polacci's results (*Abstr.*, 1900, ii, 160), obtained on distillation of leaves in a current of steam. The formaldehyde is probably liberated from its condensation products, during the distillation, as Polacci's results were obtained with dry hay, which could scarcely contain free formaldehyde.

On repeating Bach's experiments with uranium acetate (*Abstr.*, 1893, ii, 483), it was found that the solution exposed to the action of sunlight alone gave in one hour the same precipitate of uranous and uranic hydroxides as was obtained in half an hour from the solution exposed to the action of sunlight and carbon dioxide. The function of the carbon dioxide is to remove oxygen from the solution, and it may be replaced by another indifferent gas, such as hydrogen or nitrogen.

In Bach's experiments with dimethylaniline (*Abstr.*, 1903, ii, 484), no blue coloration is obtained if freshly purified dimethylaniline is used; with less pure dimethylaniline, the blue coloration is obtained from any one of the three solutions if it is insufficiently boiled and the filter insufficiently washed. G. Y.

Distribution of the Diastatic Enzymes of Green Malt. RUDOLF FÜRSTL VON TEICHEK (*Chem. Centr.*, 1904, ii, 375—376; from *Chem. Ind.*, 27, 270—275).—Examination of the diastase from the three portions of malt grain showed that the three products have approximately the same composition. The root diastase has only the dissolving power, whilst the other two both dissolve starch and produce sugar. The results confirm the theory that the twofold action of diastase is due to two ferments. N. H. J. M.

Changes of Proteids during Malting and Brewing. FR. WEIS (*Chem. Centr.*, 1904, ii, 373—374; from *Zeit. ges. Brauw.*, 27, 385—389, 405—407, 420—423, 440—445).—Proteolysis is considerable at comparatively low temperatures (4—20°), the optimum temperature being 51°, when the action is nearly twice as vigorous as at 35° and 60°. The conversion of albumoses into products which are not precipitated by tannic acid is considerably slower than the

production of albumoses, and the optimum temperature is 45—50° (probably 47—48°); no action took place in two hours at 5° and very little at 15°.

Experiments on the action of malt extracts on mashes in presence of wheat gluten showed that the rapidity of the two processes (tryptic and peptic actions) vary greatly and that the proteolytic action is influenced by temperature and by alkalis and acids; it ceases in distinctly alkaline liquids, is very weak in neutral solutions, and is helped by acid phosphates. In practice the proteolytic changes in worts may be assisted by adding proteids of other origin.

When it is desired to obtain beer with as little nitrogen as possible without withholding from the worts the necessary amides, &c., addition of malt meal would seem to be suitable.

N. H. J. M.

Effect of Sea-salt on Plants. Flora of the Salines at Cagliari. ANDREA SANNA (*Chem. Centr.*, 1904, ii, 360; from *Staz. sper. agr. ital.*, 37, 137—170).—Sea-salt is, on the whole, not injurious to the vegetation of salines. Old plants resist the action of sodium chloride better than young plants. Disease, when it occurs, is attributed to deficiency of humus or to the physical properties of the soil rather than to the amount of salt present.

N. H. J. M.

Can Lithium and Cæsium exert any Stimulant Action on Phanerogams? M. NAKAMURA (*Bul. Coll. Agr. Tōkyō*, 1904, 6, 153—157).—Lithium carbonate had a slightly stimulating action on barley and peas, and cæsium chloride (0.1 gram per kilo. of soil) slightly increased the yield of rice.

N. H. J. M.

Behaviour of Guanidine to Plants. I. KAWAKITA (*Bul. Coll. Agr. Tōkyō*, 1904, 6, 181—183).—Guanidine (0.1 per thousand) is injurious to chlorophyllous plants; biuret is somewhat less poisonous.

Fungi utilises guanidine as a source of nitrogen, but not as a source of carbon.

N. H. J. M.

Action of Sodium Nitroprusside on Plants. RANA BAHADUR (*Bul. Coll. Agr. Tōkyō*, 1904, 6, 177—179).—Sodium nitroprusside has comparatively little poisonous action on lower animals and green plants, and has no action at all on fungi in absence of light.

In the case of higher animals, it is probable that the salt is decomposed into nitrous and hydrocyanic acids.

N. H. J. M.

Peptone in Plant Seeds. W. R. MACK (*Zeit. physiol. Chem.*, 1904, 42, 259—273).—A peptone was isolated from resting lupin seeds in very small quantities. On decomposition with hydrochloric acid, it yields lysine, arginine, and glutamic acid.

W. D. H.

Milk of Castilloa Elastica. ANNE W. K. DE JONG and WILLEM R. TROMP DE HAAS (*Ber.*, 1904, 37, 3298—3301. Compare Weber, *Abstr.*, 1903, i, 845).—The milk has an acid reaction, is coagulated by methyl or ethyl alcohol, acetone, or acetic acid, but not by ammonia,

potassium hydroxide, hydrochloric acid, tannic acid or formaldehyde, whether present in small quantities or in excess. The caoutchouc obtained by coagulation is free from nitrogen.

It turns brown on exposure to the air, gives a greyish-green coloration with ferric chloride. An oxydase is not present.

The globules in the milk are not surrounded by albumin, and the coagulation is not to be attributed to the coagulation of albumin (compare Weber, *loc. cit.*). Caoutchouc appears to be soluble in ether when left in contact with the solvent for some time. A viscid solution is obtained which cannot be filtered except after dilution. Tannin is present in the milk.

J. J. S.

Cause of the Coagulation of the Milk of *Castilleja Elastica*.

ANNE W. K. DE JONG and WILLEM R. TROMP DE HAAS (*Ber.*, 1904, 37, 3301—3305).—When the crude milk is used and alcohol or acetone is employed as the coagulating agent, it is found that the quantity of coagulated caoutchouc is proportional to the amount of agent employed up to a certain maximum and then gradually decreases. With acetic acid, on the other hand, no decrease occurs after the maximum has been obtained, and even a large excess of acid causes complete coagulation. When the milk has been purified by treatment with water, it is found that alcohol and acetone behave in exactly the same manner as acetic acid.

The milk which has been purified by the aid of water is readily coagulated on boiling, whereas the crude milk is not.

The coagulation brought about by the aid of acetone, alcohol, and acetic acid is accompanied by solution of resin. The greater part of this resin is on the surface of the drops, but a small portion is also present in the interior.

J. J. S.

Examination of *Gymnema* Leaves. FREDERICK B. POWER and

FRANK TUTIN (*Pharm. J.*, 1904, [iv], 19, 234—239).—The leaves of *Gymnema sylvestre*, unlike those of *G. latifolium* (Greshoff, *Abstr.*, 1891, 338), contain no cyanogenetic glucoside. On igniting the air-dried leaves, 8.6 per cent. of ash was obtained, which yielded the following results on analysis: CaO, 19.3 per cent.; Fe_2O_3 and Al_2O_3 , 17.9 per cent.; MgO, 2.7 per cent.; the remainder consisted chiefly of alkali carbonates with traces of manganese and silica.

On adding water to an alcoholic extract of the leaves, a soft, dark green, resinous mass was obtained which contained formic and butyric acids and hentriacontane, melting at 68° and present in the leaves to the extent of about 0.05 per cent. When sulphuric acid was added to the filtrate from this precipitate, a dark-coloured resinous product was obtained. This substance, which was termed by Hooper (*Abstr.*, 1889, 723) "gymnemic acid," is a complex mixture from which ethyl acetate extracts a portion possessing the property of temporarily destroying the sense of taste for sweet substances; this latter product, for which it is proposed to reserve the name "gymnemic acid" although there is no evidence that it is a homogeneous substance, amounts to about 6 per cent. of the air-dried leaves. It has weak acidic properties and,

when fused with potassium hydroxide, yields acetic acid and a molecular compound of protocathechuic and *p*-hydroxybenzoic acids which melts at 192°; on oxidation with potassium permanganate, formic acid is produced. The resinous substance associated with the gymnemic acid in the precipitate obtained with sulphuric acid is also of an acidic nature, and yields the same products on fusion with potassium hydroxide. The liquid from which the above substances had been separated was found to contain *l*-quercitol (Trans., 1904, 85, 624) together with *i*-dextrose. The fruits of *Gymnema sylvestre* contain the same substances as the leaves with the exception of *l*-quercitol.

Gymnemic acid and the resinous substance insoluble in ethyl acetate are devoid of toxic properties. E. G.

Medicinal and Useful Plants of Brazil. THEODOR PECKOLT (*Chem. Centr.*, 1904, ii, 460; from *Ber. Deutsch. Pharm. Ges.*, 14, 308—334. Compare this vol., 142).—The abstract contains a detailed description of the quantitative composition of various parts of the following plants: *Momordica Charantia*, *Cayaponia cabocla*, *Trianosperma Martiana*, *Trianosperma diversifolia*, *Perianthopodus Espelina*, *Sicyos Martii*, *Sicyos quinquelobatus*, *Sicydium monospermum*, *Fevillea trilobata*, and *Anisosperma passiflora*. E. W. W.

Poisonous Action of Chromium Compounds on Lower Fungi, especially Saccharomycetæ. M. EMMANUEL POZZI-ESCOT (*Chem. Centr.*, 1904, ii, 350; from *Bull. Assoc. Chim. Sucre et Dist.*, 21, 1141—1142).—The poisonous effect of chromium compounds varies. In the case of the compounds tried (potassium dichromate and chromate, chromic acid, and chrome alum), chromic acid is the most and chromic salts the least poisonous. N. H. J. M.

Fungicide Actions of Cultivations of Fungi. Y. KOSAI and OSCAR LOEW (*Bul. Coll. Agr. Tōkyō*, 1904, 6, 77—79).—Vegetable cheese, known as "miso" (prepared from soy beans by means of *Aspergillus oryzae*), when kept in an open beaker at a temperature which was allowed to rise to 33—35°, showed successively developments of yeast, *Sarcina*, and *Bacillus prodigiosus*. No traces of *Aspergillus* or *Penicillium* appeared. The substance finally became alkaline.

Further experiments showed that *Aspergillus oryzae* (grown in solutions containing peptone, sugar, potassium dihydrogen phosphate, and magnesium sulphate) produces a fungicide substance which, however, is not equally injurious to all fungi.

Penicillium spores sown in slightly alkaline cultures of *Bacillus pyocyaneus* failed to develop. N. H. J. M.

Treatment of Crops by Stimulating Compounds. OSCAR LOEW (*Bul. Coll. Agr. Tōkyō*, 1904, 6, 161—175).—A summary of the results obtained during the last three years. Manganese salts are probably beneficial in promoting the action of oxidising enzymes in changing noxious by-products of metabolism by partial oxidation.

Of the various stimulants tried, only manganese, fluorine, and iodine compounds promise to be of agricultural importance. Ferrous compounds also deserve attention, and Molisch has shown that iron is not only concerned in producing chlorophyll.

Having regard to the injurious action on crops of any excess of iodides and fluorides, it is recommended to restrict the employment of stimulants to manganous salts, which should be applied only in top-dressing (about 25 kilos. per hectare), in high dilution and in conjunction with ferrous sulphate (about 20 kilos. per hectare).

N. H. J. M.

Development of Rye and Wheat. BERNHARD SCHULZE (*Chem. Centr.*, 1904, ii, 790—791; from *Landw. Jahrb.*, 33, 405—441).—Rye acquired nearly half the total nitrogen by the end of winter. In the case of wheat, the nitrogen-assimilation took place chiefly from the end of April to the commencement of grain-formation. A good deal of potassium is taken up in the winter, especially in the case of rye, but most of it is assimilated at the time when carbohydrates are produced in greatest quantity. Calcium and magnesium are required only in small amounts by the young plants, and their utility, like that of silica, may presumably be connected with the strengthening of the tissues. Phosphoric acid is taken up during the period of growth in the spring and later.

N. H. J. M.

Influence of Different Ratios of Lime to Magnesia on the Growth of Rice. KEIJIRŌ ASŌ (*Bul. Coll. Agric. Tōkyō*, 1904, 6, 97—102).—The lime factor for rice is about 1, being similar to that of other gramineous crops, which is between 1 and 2, but the yield of rice is less diminished by an excess of magnesium than by a similar excess of calcium.

N. H. J. M.

Action of Different Forms of Nitrogen, especially Ammonia and Sodium Nitrate, on Potatoes and Oats. WILHELM SCHNEIDEWIND and DIEDRICH MEYER (*Chem. Centr.*, 1904, ii, 787—788; from *Landw. Jahrb.*, 33, 335—342).—Ammonium salts gave better results with potatoes than does sodium nitrate. With oats, the dry matter produced was somewhat less with ammonium salts than with sodium nitrate. Ammoniacal nitrogen is utilised more economically. The less intensively nitrogen acts, the greater the amount of organic matter produced by an equal amount of nitrogen assimilated, and *vice versa*.

N. H. J. M.

Different Behaviour of Potatoes and Mangolds towards Crude and Pure Potassium Salts. WILHELM SCHNEIDEWIND and DIEDRICH MEYER (*Chem. Centr.*, 1904, ii, 788—789; from *Landw. Jahrb.*, 33, 347—353).—Sodium chloride, the chief impurity of Stassfurt potassium salts, slightly increased the yield of potatoes when employed in conjunction with a small amount of potassium, but in presence of an abundance of potassium considerably diminished the yield. In similar experiments with mangolds, the yield was increased

in both cases, especially the latter. Kainite is less suitable for potatoes and better for mangolds than the pure salts.

Potassium silicate and carbonate gave the worst results with potatoes, whilst for mangolds they are not inferior to the pure sulphate and chloride. N. H. J. M.

Can Salts of Zinc, Cobalt, and Nickel in High Dilution exert a Stimulant Action on Agricultural Plants? M. NAKAMURA (*Bul. Coll. Agr. Tōkyō*, 1904, 6, 147—152).—In experiments with *Allium* manured with zinc sulphate, nickel sulphate, and cobalt nitrate respectively (0.01 gram in 2 to 2.3 kilos. of soil), a slightly stimulating effect was observed in each case. With *Brassica chinensis*, nickel and cobalt slightly increased the leaf production, but not the roots. *Hordeum*, which was grown after *Brassica* without further application, was slightly stimulated by cobalt, whilst nickel and zinc proved to be injurious, although present in very small quantities. In experiments with peas, zinc was without effect, whilst cobalt and nickel had no very appreciable action. N. H. J. M.

Influence of Manganese on Trees. OSCAR LOEW and SEIROKU HONDA (*Bul. Coll. Agr. Tōkyō*, 1904, 6, 126—130).—Manganese sulphate applied to *Cryptomeria japonica* more than doubled the weight of the trees in 18 months. Ferrous sulphate and sodium nitrate had some effect in promoting the growth of twigs, whilst sodium chloride much reduced the growth. N. H. J. M.

Influence of Manganese Salts on Flax. Y. FUKUTOME (*Bul. Coll. Agr. Tōkyō*, 1904, 6, 136—137).—The joint application of iron and manganese had a distinct effect in increasing the yield of flax, whilst separately they had less effect. Cobalt nitrate (0.02 gram in 8 kilos. of soil) had also a stimulating effect. N. H. J. M.

Chemistry of Fruits. KARL WINDISCH and KARL BOEHM (*Zeit. Nahr. Genussm.*, 1904, 8, 347—352).—The total nitrogen, nitrogen as proteids, amides, and ammonia, pectin substances, tartaric acid, and sugar, were determined in a number of fruits.

In red currants, gooseberries, bilberries, cranberries, quinces, wild pears, and medlars, the whole of the sugar was found to be invert sugar, and this was also the predominating sugar in black currants, mulberries, morella cherries, pears, apples, and sloes. Peaches contained 3.17 per cent. of sucrose and 1.02 per cent. of invert sugar. The greatest amount of total sugar was found in sloes (13.48 per cent.), and the least in peaches (4.19 per cent.). N. H. J. M.

Analyses of Fresh Chestnuts. Their Food Value and Manurial Requirements. BERTANI TOMEI (*Chem. Centr.*, 1904, ii, 346; from *Staz. sper. agrar. ital.*, 37, 185—199).—Two samples of fresh, peeled chestnuts (*a* and *b*) contained water, (*a*) 53.75 and (*b*) 11.80; dextrose, (*a*) 0.505 and (*b*) 1.204; sucrose, (*b*) 4.756; tannin, (*a*) 0.9; crude proteid, sol. in water, (*b*) 1.131; pure proteid, sol. in water, (*b*)

0.103; starch, (a) 8.010 and (b) 8.739; fat, (a) 1.83 and (b) 1.984; insoluble crude proteid, (a) 3.348 and (b) 5.231; insoluble pure proteid, (a) 2.428 and (b) 3.881; digestible proteid (insoluble), (b) 1.669. The ash constituents in (b) were as follows:

| Pure ash. | CO ₂ . | K ₂ O. | Na ₂ O. | P ₂ O ₅ . | SO ₃ . | SiO ₂ . |
|-----------|-------------------|-------------------|--------------------|---------------------------------|-------------------|--------------------|
| 1.200 | 0.406 | 0.274 | 0.399 | 0.219 | 0.100 | 0.014 |

The nutritive value is small.

N. H. J. M.

Distilled Grape Residues. CARLO MENSIO and U. SOMMA (*Chem. Centr.*, 1904, ii, 610; from *Staz. sper. agrar. ital.*, 37, 392—397).—Two samples of the distilled residues from pressed grapes, the one (a) with stones and the other (b) without stones, were found to contain respectively 56.98 and 59.10 per cent. of water, 4.74 and 4.08 of crude proteid, 0.76 and 0.653 of nitrogen, 3.62 and 2.53 of fat, 19.88 and 19.60 of cellulose, 2.21 and 1.83 of pentosans, 10.50 and 9.16 of extractives free from nitrogen, 2.07 and 3.70 of mineral matter, 0.206 and 0.175 P₂O₅, and 0.328 and 0.478 K₂O. Both these materials might be used as fodder or as manure, the residues containing the stones being the more valuable.

E. W. W.

Culture Experiments on the Action of Calcium Fluoride on Vesuvian Soil. GASPARE AMPOLA (*Gazzetta*, 1904, 34, ii, 156—165).—The soil employed in these experiments, as is very commonly the case in Italy, was very poor in potassium, the total potassium oxide being 42.13, that soluble in water 1.04, and that soluble in 5 per cent. acetic acid 2.83 parts per thousand of the soil. The land was manured with superphosphate and sodium nitrate, and varying amounts of calcium fluoride were applied. It was found that the crops were greatly increased by the use of calcium fluoride, and so also was the amount of potassium assimilated by the crops. The action of this salt is explained by the author as follows: the calcium fluoride is decomposed by very feeble organic acids, for example, carbonic acid, with liberation of hydrofluoric acid, which then acts on the complex silicates and renders the potash assimilable.

T. H. P.

Can Plant Analyses disclose the Amount of Assimilable Nutritive Substances in the Soil? M. STAHL-SCHRÖDER (*J. Landw.*, 1904, 52, 193—268).—In seasons with low rainfall, the nitrogen, and in a less degree the phosphoric acid, of oat grain increases. The numbers showing the relations between nitrogen and phosphoric acid proposed by Atteberg as indications of deficiency of nitrogen and phosphoric acid in the soil are not directly available for countries other than Sweden. In Courland the relation N:P₂O₅ is 100:30—40 in oat grain. Grain from the south-east of Russia contains more nitrogen and more phosphoric acid, the increase in the nitrogen being the greater.

The bases in oat grain give very little information as to the condition of the soil.

As regards oat-straw, increasing one manure constituent did not, as a rule, cause a diminution in the amounts of other constituents in the straw. A high percentage of potassium in straw indicates an abundance in the soil, but a low percentage does not necessarily indicate a deficiency in the soil. If, however, the low percentage of potassium in straw is coincident with high percentages of sodium, calcium, and magnesium, the conclusion to be drawn is that the soil is poor in assimilable potassium.

In the concluding portion of the paper, the methods of Joulie, Helmkamp, Ville, and Wilfurth are discussed. N. H. J. M.

Determination of the Available Amounts of Lime and Magnesia in the Soil. T. KATAYAMA (*Bul. Coll. Agr. Tôkyô*, 1904, 6, 103—124).—The results of sand-culture experiments and experiments with two widely differing soils showed that, with onions, the best results are obtained when the relation $\text{CaO} : \text{MgO} = 2 : 1$.

The method employed for determining the available lime and magnesia is as follows: the particles of soils smaller than 0.25 mm. are separated and extracted for 50 minutes with 10 per cent. hydrochloric acid—50 c.c. acid to 25 grams of soil. Water (200 c.c.) is then added, and the diluted liquid boiled for 10 minutes longer and filtered after 15 hours. N. H. J. M.

Action of Calcium Cyanamide on Peat Soils BRUNO TACKE (*Bied. Centr.*, 1904, 33, 583—584; from *Mitt. Ver. Förd. Moorkultur*, 1903, No. 23, 347).—Crude calcium cyanamide contains 14—23 per cent. of nitrogen, and was shown by Gerlach and Wagner's pot and field experiments to have a manurial value almost equal to that of sodium nitrate.

The results of pot experiments in which mustard was grown in peaty soil showed that less dry produce was obtained after application of calcium cyanamide than when no nitrogen was applied. A poisonous action was observed when the manure was added just before sowing the seed, but not when there was an interval of two-and-a-half months. N. H. J. M.

What Forms of Phosphoric Acid are Suitable for Manurial Purposes? PAUL WAGNER (*Bied. Centr.*, 1904, 33, 513—515; from *Saaten-Dünger u. Futtermarkt.*, 1904, No. 5, 50).—The citrate-soluble phosphoric acid of bone-precipitate was found to be equal to that of basic slag, and both of these nearly equalled water-soluble phosphate.

Experiments with the precipitated phosphoric acid of double superphosphate, extending over nine years, showed that the citrate-soluble phosphoric acid was less active than water-soluble phosphoric acid, and that it was not assimilated by the plants (summer rye) with sufficient rapidity. In the second and subsequent years, however, its activity approached very nearly to that of water-soluble phosphoric acid. N. H. J. M.

Manurial Value of Dried Superphosphate. ACH. GRÉGOIRE and J. HENDRICK (*Chem. Centr.*, 1904, ii, 555; from *Bull. Stat. agric. Gembloux*, 74, 33—49).—Results of experiments with barley showed that the physical changes in superphosphate dried at 165° are without effect on the manurial value and that the action of the phosphoric acid is distinctly increased. Monocalcium phosphate, deprived of 2 mols. H₂O by heating at 165°, gave better results than the crystallised salt dried at 70°. The metaphosphate and the pyrophosphate prepared by completely driving off the water from the mono- and di-phosphates respectively have no manurial value. N. H. J. M.

Phosphatic Slags. ACH. GRÉGOIRE and J. HENDRICK (*Chem. Centr.*, 1904, ii, 555; from *Bull. Stat. agric. Gembloux*, 74, 50—57).—The action of 100 c.c. of a solution containing 21 per cent. citric acid, 4·3 per cent. of nitrogen as ammonia, 3 per cent. of ammonium fluoride and 2 per cent. of calcium nitrate on 1 gram of basic slag varied considerably, the results being but little influenced by heating at 70° instead of at 100° or by heating for 2 hours instead of 1 hour. The solution had hardly any effect on Martin slag and mineral phosphate. Pot experiments with barley showed that the phosphoric acid insoluble in the solution containing fluoride was not less active than the unchanged slags, whilst the phosphoric acid undissolved by 2 per cent. citric acid is distinctly less assimilable. N. H. J. M.

Action of the Phosphoric Acid of Fæces. Comparison of Wolter Phosphate with Superphosphate and Basic Slag. WILHELM SCHNEIDEWIND and DIEDRICH MEYER (*Chem. Centr.*, 1904, ii, 788; from *Landw. Jahrb.*, 33, 342—347).—Horse dung and cow dung gave very good results with mustard, corresponding with the solubility of the phosphoric acid soluble in citric acid. In pot experiments with oats, cow dung was even better than superphosphate, probably owing to other constituents of the dung.

Wolter phosphate gave, in pot experiments with mustard and oats, about the same results as superphosphate, and its after effect was somewhat greater than that of superphosphate. Less phosphoric acid was taken up from Wolter phosphate than from superphosphate, but more than from basic slag. N. H. J. M.

Action of Crude and Pure Potassium Salts with Different Forms of Calcium. WILHELM SCHNEIDEWIND and O. RINGLEBEN (*Chem. Centr.*, 1904, ii, 789; from *Landw. Jahrb.*, 33, 353—371).—When soil is deficient in calcium carbonate, potassium chloride and sulphate act better than kainite; otherwise kainite gave the best results. Gypsum was injurious to a mixture of clover and grasses, especially when kainite was applied. Oats were less affected, whilst potatoes were benefited by gypsum.

The action of sodium cannot be attributed only to its taking the place of potassium, inasmuch as it increases the yield in presence of a large excess of potassium. This may be due to the production of sodium

nitrate and phosphate, and to the greater diffusibility of those salts as compared with the salts of other bases.

The chlorine of manures is deposited chiefly in the straw of cereals and in the leaves of root-crops.

N. H. J. M.

Composition of the Incrustations in Roberts-Concentrators.

GIUSEPPE ONGARO (*Chem. Centr.*, 1904, ii, 361—362; from *Staz. sper. agrar. ital.*, 37, 231—233).—The incrustation, obtained from a tobacco factory in Venice, was a yellowish-red powder containing water, 8.466; organic matter, 37.822; and ash, 53.712 per cent. The substance contains a good deal of readily assimilable phosphoric acid and nitrogen, and is suitable for manuring.

N. H. J. M.

Analytical Chemistry.

Continuous-Observation Polarimeter Tube. JOHN SIMPSON FORD (*Analyst*, 1904, 29, 281—282).—The 200 mm. tube described is made entirely of metal with glass end-plates secured by screw-caps as usual. At one end of the tube is fixed a conical funnel of about 65 c.c. capacity, and at the other a discharge pipe. The solution to be observed is poured into the funnel to fill the tube. After taking the reading, a second solution may be poured into the funnel and so on. Each successive solution quickly washes the previous one out of the tube, even when they are of different specific gravities.

W. P. S.

The Material and Shape of the Rotating Cathode. HERBERT E. MEDWAY (*Amer. J. Sci.*, 1904, [iv], 18, 180—182. Compare Abstr., 1903, ii, 613).—A silver crucible may be employed as a rotating cathode for the deposition of metals, the results obtained being as accurate as when platinum is employed. Deposited copper is removed by rubbing and finally by treatment with boiling hydrochloric acid. A nickel cathode is attacked, both during the process and in the subsequent removal of the deposit, causing inaccurate results. No coherent deposit can be obtained on aluminium.

The disc form of cathode is inferior to the crucible form in retaining the deposit.

C. H. D.

Bunsen Burners and Combustion Apparatus without Gas. HARRY DRAKE GIBBS (*J. Amer. Chem. Soc.*, 1904, 26, 760—764).—An arrangement for burning the vapour of alcohol (or other liquid combustibles) in Bunsen burners. For details, the original paper and drawings should be consulted.

L. DE K.

Mixed Indicators. MAX SCHOLTZ (*Zeit. Elektrochem.*, 1904, 10, 549—553).—If a solution of *p*-nitrophenol and phenolphthalein in hydrochloric acid is neutralised by potassium hydroxide solution, the yellow colour of the nitrophenol ion first appears and then the pink colour of the phenolphthalein. The nitrophenol is therefore a stronger acid than the phenolphthalein. In a similar way, all the indicators may be compared. The following is the order found by the author, beginning with the strongest acid: (1) alizarinsulphonic acid, iodoeosin; (2) *p*-nitrophenol; (3) luteol; (4) hæmatoxylin, rosolic acid; (5) litmus; (6) turmeric; (7) phenolphthalein. Some other indicators which give less sharp colour changes are the following.

Alizarin lies between *p*-nitrophenol and litmus, fluorescein lies between iodoeosin and litmus, and tropæolin 000 between luteol and litmus.

Cochineal and phenacetolin are stronger than litmus, gallein is stronger than *p*-nitrophenol, lacmoid is stronger than turmeric, and brazilin and α -naphtholbenzein are weaker than luteol and litmus respectively. Among the basic indicators, cyanine is a stronger base than methyl-orange or the tropæolins. T. E.

Application of Potassium Tetraoxalate in Titration. GEORG LUNGE (*Chem. Zeit.*, 1904, 28, 701—702).—A reply to Kühling's criticisms (*ibid.*, 596, 612) of a previous paper (this vol., ii, 289). The author has never been able to prepare a potassium tetraoxalate in which the water of crystallisation corresponds accurately with the formula $C_2O_4HK, C_2O_4H_2, 2H_2O$; on the other hand, sodium carbonate and sodium tetraoxalate giving an analytical error of less than 0.1 per cent. can readily be obtained. W. A. D.

Use of Potassium Iodate for the Detection and Estimation of Iodides, Bromides, and Chlorides. STANLEY BENEDICT and J. F. SNELL (*Chem. Zeit.*, 1904, 28, 729).—In reply to criticisms, the authors state that they were unaware of the process of Ditz and Margosches (this vol., ii, 145) published previously, and also that their method differs in several particulars from that of Bugarszky, as the use of potassium iodate permits of the estimation of chlorides, bromides, and iodides in the presence of each other. W. P. S.

Estimation of Iodine in the presence of Bromine and Chlorine. E. THILO (*Chem. Zeit.*, 1904, 28, 866).—The process is based on the fact that when silver nitrate is gradually added to a solution containing iodides, bromides, and chlorides, the iodine is precipitated first, followed by the bromine and then by the chlorine.

The solution is therefore titrated with *N*/10 silver nitrate until a drop of the liquid no longer gives a dark spot on paper impregnated with a weak solution of palladium chloride. The filtrate may be titrated for total bromine and chlorine as usual, using potassium chromate as indicator. If bromine only is to be estimated, it is sufficient to add enough *N*/10 silver nitrate to convert all the bromine with a portion of the chloride into the silver salts, which are then

weighed in the usual manner. As the amount of metallic silver contained therein is of course known from the number of c.c. of silver solution added, the amount of silver bromide may be calculated easily.

Commercial iodine and cuprous iodide may be converted into soluble zinc iodide by trituration with zinc dust and water. If the silver iodide does not separate readily, a little salt may be added.

L. DE K.

Estimation of Fluorine in Martin Slag. L. FRICKE (*Chem. Centr.*, 1904, ii, 728—729; from *Stahl u. Eisen*, 24, 889—890).—In order to determine the quantity of fluorine in Martin slag, 5 grams of the powdered slag mixed with 5—6 times the quantity of potassium carbonate are kept molten in a platinum crucible at a good heat for $\frac{1}{2}$ —1 hour. After extracting the cold mass with hot water and filtering, the silica and alumina are precipitated by prolonged boiling with ammonium carbonate. The filtrate is heated with a solution of zinc oxide in ammonia, evaporated to dryness, and heated to 120°. The residue is taken up with cold water and the zinc phosphate, carbonate, and silicate filtered off and washed with a 2 per cent. solution of potassium carbonate. To the filtrate, 1—1.5 grams of calcium chloride are added, it is then acidified with acetic acid, and the carbon dioxide removed by warming the solution. The solution is made alkaline with potassium hydroxide solution, and again faintly acid with acetic acid. The precipitate, which consists of calcium fluoride together with some calcium phosphate, is collected, washed with cold water until no more calcium can be detected in the washings, and finally ignited and weighed. It is then warmed with concentrated sulphuric acid in the platinum crucible, diluted, ammonia added until only faintly acid, and the phosphoric acid precipitated by molybdic acid. If only a small quantity of precipitate is formed, the phosphoric acid is estimated by titrating with lead acetate, but if the precipitate is larger it is dissolved and precipitated with magnesia mixture. The percentage of fluorine x may be calculated from the formula $x = 48.72/s.(a - 1.392d)$, in which a = weight of calcium fluoride and phosphate, d = weight of magnesium pyrophosphate, and s = weight of substance taken. The result may be checked by making the filtrate from the phosphomolybdic acid precipitate up to 250 or 500 c.c. and determining the quantity of calcium in 100 or 200 c.c. respectively. If c = weight of CaO, then $x = 67.857/s.(c - 0.7543d)$.

E. W. W.

Estimation of Water in Substances which afterwards are to be extracted with Volatile Solvents. ROBERT M. BIRD (*J. Amer. Chem. Soc.*, 1904, 26, 818—826).—An arrangement chiefly devised for the estimation of water and fat in butter. The sample is introduced into a weighed Gooch crucible and dried in a current of hot air for 20—30 minutes; the loss in weight represents the water. The fat is then removed by extracting with ether for about half an hour, and the crucible is reweighed; the loss represents the fat. For full particulars of the apparatus, which admits of five estimations being conducted simultaneously, the original paper and drawings should be consulted.

L. DE K.

Application of Hydrazine Sulphate in the Determination of Oxidising Substances. U. ROBERTO and F. RONCALI (*Chem. Centr.*, 1904, ii, 616; from *L'Ind. Chim.*, 6, 178—179).—Hydrazine sulphate acts with substances which liberate oxygen in precisely the same way as it does with chlorine (compare *ibid.*, 93), being decomposed by the oxygen and yielding sulphuric acid, water, and nitrogen. When potassium permanganate is gently heated with hydrazine sulphate, the solution is decolorised and nitrogen is evolved, 5 mols. of nitrogen being liberated by 4 of permanganate. In a similar way, 2 mols. of potassium dichromate yield 3 mols. of nitrogen. By measuring the volume of nitrogen liberated, the quantity of oxidising substance may be estimated. This method is also applicable to peroxides, chlorates, &c. E. W. W.

Forms in which Sulphur exists in Coal; their Effects on the Heating Power. E. E. SOMERMEIER (*J. Amer. Chem. Soc.*, 1904, 26, 764—780).—The author has studied the influence of the sulphur in coals on their heating powers as calculated by Dulong's formula, and arrived at the following conclusions.

For sulphur present as ferrous sulphate, there is a loss of 10 cal. for each per cent. of sulphur. When the sulphur is present as iron pyrites, the result is too high by about 9.6 cal. for each per cent. on uncorrected ultimate analyses. On corrected analyses (where a correction has been made for oxygen in the ash), the results are too low by 6.6 cal. When the sulphur exists in an organic combination, there is a loss of about 4.5 cal. for each per cent. so present.

L. DE K.

Photometric Estimation of Sulphur in Coal. SAMUEL W. PARR and C. H. MCCLURE (*J. Amer. Chem. Soc.*, 1904, 26, 1139—1143).—A description of an improved photometer used for the determination of small quantities of sulphates by means of barium chloride (compare Jackson, *Abstr.*, 1902, ii, 172). For particulars, the illustration and table of the original paper should be consulted.

L. DE K.

Estimation of Sulphur in Iron. ALLEN P. FORD and OGDEN G. WILLEY (*J. Amer. Chem. Soc.*, 1904, 26, 801—808).—The following process, originally proposed by Bamber, is recommended as being particularly suitable for analysts who have but limited experience in sulphur estimations. Two grams of the drillings are dissolved in nitric acid contained in a platinum dish covered with a watch-glass. When solution is complete, 1 gram of nitre is added, the liquid is evaporated to dryness, and the residue heated to redness for 3 or 4 minutes. The mass is now boiled with 50 c.c. of a 1 per cent. solution of sodium carbonate and the residue washed with the same hot liquid. The filtrate is freed from nitric acid by evaporating with hydrochloric acid, and the dry residue dissolved in 50 c.c. of water and 2 c.c. of hydrochloric acid. The sulphuric acid is then estimated as usual with barium chloride.

L. DE K.

Estimation of Sulphur in Pig-iron and Steel by Titration with Iodine and Thiosulphate Solution. L. FRICKE (*Chem. Centr.*, 1904, ii, 727—728; from *Stahl u. Eisen.*, 24, 890—891).—In order to estimate the quantity of sulphur in pig-iron or steel, 100 c.c. of water and 75 of concentrated hydrochloric acid are added, by means of a separating funnel, to 10 grams of steel or 5 of iron contained in a $\frac{1}{2}$ —1 litre flask which is fitted with a condenser and receiver. The mixture is heated moderately. The water and hydrochloric acid vapours are mostly condensed, whilst the hydrogen sulphide passes through a dry vessel and then successively into three vessels of which the last two contain a solution of 25 grams of cadmium acetate in 200 c.c. of glacial acetic acid. The gas is finally expelled from the apparatus by carbon dioxide and the contents of the receiver are diluted to about 150 c.c. with the cadmium solution and titrated. For this purpose, iodine and sodium thiosulphate solutions are used, of which 1 c.c. corresponds with 1 mg. of sulphur (these solutions contain respectively 7.928 grams of iodine and 25 of potassium iodide, and 15.526 of thiosulphate and 2 of ammonium carbonate per litre). Excess of iodine solution is added to the cadmium sulphide together with 75 c.c. of a solution of 300 c.c. of concentrated hydrochloric acid in 850 c.c. of water (sp. gr. 1.124), and the excess of iodine titrated with sodium thiosulphate after adding 2 c.c. of an iodine-zinc-starch solution. The difference between the amounts of iodine and thiosulphate solution used gives the percentage of sulphur. E. W. W.

Estimation of Sulphur and Phosphoric Acid in Foods, Fæces, and Urine. J. A. LE CLERC and WILBUR L. DUBOIS (*J. Amer. Chem. Soc.*, 1904, 26, 1108—1113).—The authors have used the calorimetric processes of Berthelot and Parr, and also the sodium peroxide process recommended by Osborne (*Abstr.*, 1902, ii, 223), and are in favour of the latter method.

Tables are given showing the amount of sulphur in various foods and dried fæces. In the case of urine, the direct titration of the phosphoric acid in the diluted sample with uranium acetate is preferred to the combustion processes. L. DE K.

Estimation of Sulphuric Acid in Urine by Alcoholic Strontium Chloride. ROLAND VON LENGYEL (*Pflüger's Archiv*, 1904, 104, 514—518).—The estimation of sulphuric acid in the urine by an alcoholic solution of strontium chloride instead of barium salts is recommended. The new method is correct and rapidly carried out. W. D. H.

Estimation of Sulphuric Acid in presence of Iron. FRIEDRICH W. KÜSTER (*Zeit. angew. Chem.*, 1904, 17, 1180).—Silberberger concludes that sulphuric acid cannot be estimated in presence of iron by Lunge's method, and, in support of his contention, quotes Küster and Thiel (*Abstr.*, 1899, ii, 247); Küster on the contrary holds that Lunge's method gives accurate results. A. McK.

Estimation of the Active Oxygen in Organic Persulphates. A. WOLFF and RICHARD WOLFFENSTEIN (*Ber.*, 1904, **37**, 3213—3214).—The method consists in adding sulphurous acid to the solution of the organic persulphate, whereby the sulphurous acid is oxidised to sulphuric acid, which is then estimated as barium sulphate.

E. F. A.

Comparison of the Gravimetric Methods for Estimating Selenium. ALEXANDER GUTBIER, G. METZNER, and JUL. LOHMANN (*Zeit. anorg. Chem.*, 1904, **41**, 291—304).—The majority of the gravimetric methods for estimating selenium are based on the use of reducing agents. The methods described were conducted with selenium dioxide, which was specially purified. Details are given of the reduction of selenium dioxide by hydrazine hydrate, hydrazine hydrochloride, hydrazine sulphate, sulphurous acid, sodium sulphite, ammonium sulphite, hydroxylamine hydrochloride, hydriodic acid, and hypophosphorous acid respectively. These various methods all yield good results. The methods recommended are those with hydrazine hydrate, hydrazine sulphate, hydrazine hydrochloride, and sulphurous acid.

A. McK.

Estimation of Tellurium by Electrolysis. GIOVANNI PELLINI (*Atti R. Accad. Lincei*, 1904, [v], **13**, ii, 275—277).—The author has further tested the method devised by him for the estimation of tellurium (this vol., ii, 147), by dissolving a known weight of pure redistilled tellurium in nitric acid, evaporating the nitric acid, adding concentrated sulphuric acid and ammonium hydrogen tartrate, and electrolysing as previously described. The results obtained have errors varying from about 0.08 to 0.16 per cent. It is found that quantities of tellurium much greater than 1 gram can be deposited, so that the method may be used for the purification of this element. T. H. P.

Estimation of Organic Nitrogen by Sodium Peroxide. FRITZ VON KONEK and ARTHUR ZÖHLIS (*Zeit. angew. Chem.*, 1904, **17**, 1093—1095).—Organic substances are not, as a rule, quantitatively converted into nitric acid by sodium peroxide. The method gives good results, however, when applied to the estimation of nitrogen in flour.

The flour, dried at 100—102°, is mixed in a steel cylinder with an excess of dry sodium peroxide, to which a mixture of potassium persulphate and tartaric acid had been added. The cylinder is kept cool in water, and when the vigorous oxidation, which is started by means of a red-hot iron wire, is complete the whole is dissolved in water. The nitrate is then reduced to ammonia by the addition of pumice, alcohol, and Devarda's alloy of aluminium and copper, and the ammonia estimated as in the Kjeldahl process. Results obtained from various specimens of flour by this method and by Kjeldahl's are in close agreement.

A. McK.

Use of Sodium Peroxide in Analysis. HANS H. PRINGSHEIM (*Zeit. angew. Chem.*, 1904, **17**, 1454—1455).—A reply to von Konek

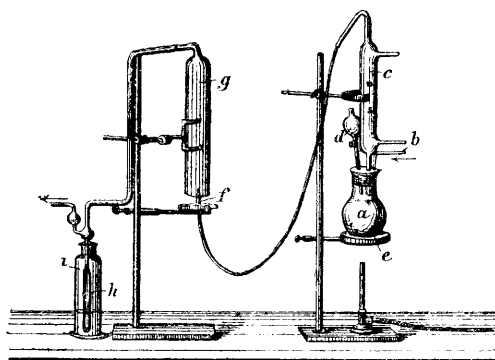
(preceding abstract). As regards the nitrogen, up to 90 per cent. may be liberated as such during the combustion. L. DE K.

Estimation of Phosphorus in Solutions. ANASTASIOS C. CHRISTOMANOS (*Zeit. anorg. Chem.*, 1904, 41, 305—314. Compare this vol., ii, 614).—When a solution of yellow phosphorus in ether or in benzene is agitated with copper nitrate solution for a few seconds, a black precipitate is formed, which consists, not of the compound Cu_3P_2 , but of mixtures of Cu_3P_2 and Cu_6P_2 , approximating to the composition Cu_5P_2 . The composition is, however, very variable and the precipitate is often highly oxidised.

In the method of estimation described, an ethereal solution of phosphorus is heated for several minutes with a 10 per cent. solution of copper nitrate, of which so much is taken that the solution remains blue after the black precipitate has subsided. The ether is then expelled and the product oxidised by bromine, when the actions represented by the equations: $\text{Cu}_6\text{P}_2 + \text{Br}_{12} = 3\text{Cu}_2\text{Br}_2 + 2\text{PBr}_3$ and $\text{Cu}_6\text{P}_2 + \text{Br}_{10} = \text{Cu}_2 + 2\text{Cu}_2\text{Br}_2 + 2\text{PBr}_3$, take place. After removal of the excess of bromine, the copper is separated as sulphide and the phosphorus determined by the addition of magnesia mixture in the usual manner.

A. MCK.

Estimation of Phosphorus in Calcium Carbide. HJ. LIDHOLM (*Zeit. angew. Chem.*, 1904, 17, 1452).—Ten grams of the powdered sample are put into a crucible, which is then placed into the 500 c.c. flask, *a*.



A current of hydrogen is passed through the tube *b*, and when the air has been expelled the burner, *f*, is lit and the pump, attached to the exit tube of the wash-bottle *h*, put into action. After fitting on the condenser, 30 c.c. of absolute alcohol are introduced drop by drop

through the funnel, *d*, and the same volume of water is then cautiously added. Any hydrogen phosphide formed will burn together with the hydrogen, and acetylene and the phosphoric acid will deposit partly on the sides of the cylinder, *g*, and partly find its way into the wash-bottle, *h*. When evolution of acetylene has ceased, hydrochloric acid is added to dissolve the calcium hydroxide, and the liquid is heated to boiling so as to expel the last traces of phosphorus compounds.

The cylinder, wash-bottle, &c., are then rinsed with dilute ammonia and the phosphoric acid is precipitated as usual with magnesia-mixture.

L. DE K.

Estimation of Phosphoric Acid in Aqueous Extracts of Soils and Plants. OSWALD SCHREINER (*J. Amer. Chem. Soc.*, 1904, 26, 808—813).—The colorimetric process for the estimation of phosphoric acid in the presence of silica (this vol., ii, 85) has been found useful for the estimation of small quantities of phosphoric acid in aqueous solutions of soils and plants. If the solutions are not quite colourless, the colour should be removed by treatment with carbon black.
L. DE K.

Official Tests for Arsenic. WYNDHAM R. DUNSTAN and HENRY H. ROBINSON (*Pharm. J.*, 1904, [iv], 19, 381—382, 405—407, 426—427, 448—450).—Instructions are given for applying Mayençon and Bergeret's test (Abstr., 1874, 1008), which depends on the yellow stain produced by arsenic hydride on mercuric chloride paper, to the drugs of the B. P. The stain given by 0.012 mg. of arsenic is used as a standard for comparison. When 4 grams of the drug are employed in the test, this stain represents 3 parts of arsenic per million. It is considered that for most drugs which are administered in small doses, the amount of arsenic present should be less than 3 parts per million, whilst in the case of tartaric and citric acids the quantity present should be less than 1 part per million, for the principal mineral acids, 3/10 part per million, and for solution of ammonia, 1/10 part per million. Special directions are given for the application of the test to a number of drugs which offer particular difficulties.
E. G.

Electrolytic Methods for the Detection and Approximate Estimation of Minute Quantities of Arsenic in Beer, Malt, and Food-stuffs, &c. WILLIAM THOMSON (*Mem. Proc. Manchr. Lit. Phil. Soc.*, 1904, 48, xvii, 1—14).—The author has experimented on the use of various cathodes in the electrolytic estimation of arsenic. With lead, smaller quantities of arsenic could be detected than with platinum, but the results were irregular; with aluminium and plumbago, 50 c.c. of a solution containing 1/500 grain per gallon gave no mirror, whilst tin was not procured sufficiently free from arsenic.

A form of apparatus in which pure zinc serves as a cathode is recommended and described in the paper. A comparison between it and the apparatus recommended by the Royal Commission is given, in respect to the influence of amyl alcohol and invert sugar on the production of the mirror. The preliminary reduction of arsenic to arsenious compounds is not necessary.
G. D. L.

Estimation of Boric Acid in Cider, Fruits, &c. ALFRED H. ALLEN and ARNOLD R. TANKARD (*Pharm. J.*, 1904, [iv], 19, 242—244).—The presence of boric acid in cider and fruits can be detected by the following method. The ash obtained by evaporating 20 c.c. of cider or apple juice to dryness and igniting the residue, or by directly igniting 25 grams of the fruit, is acidified with dilute hydrochloric acid; a piece of turmeric paper is immersed in the liquid and the mixture is evaporated to dryness. If boric acid is present, the turmeric paper assumes a brownish-red colour, which is changed to a

variety of colours, chiefly green and purple, when moistened with solution of sodium hydroxide.

The following method is recommended for estimating the boric acid. About 100 c.c. of cider or fruit juice are treated with a few c.c. of 10 per cent. calcium chloride solution and evaporated to dryness, or a quantity of the fruit (about 50 grams) is cut into small pieces and a solution of calcium chloride poured over the mass, which is afterwards dried. The dry residue is well charred and then boiled with 150 c.c. of water and the liquid filtered. The carbonaceous residue is incinerated at a moderate temperature and afterwards boiled with 150 c.c. of water and left for a few hours. The liquid is then filtered and the filtrate added to the first extract. The mixed filtrates are evaporated to 25—30 c.c. and, when cold, are neutralised with $N/10$ acid, methyl-orange being used as indicator. An equal volume of glycerol is now added and the liquid is titrated with $N/20$ sodium hydroxide in presence of phenolphthalein. A further quantity of glycerol (about 10 c.c.) is added, and the titration continued until a permanent red coloration is produced. Each c.c. of $N/20$ sodium hydroxide required represents 0.0031 gram of boric acid.

An alternative method for the estimation of boric acid is given. The substance is treated with calcium chloride in the manner already described, and is afterwards charred and extracted with about 50 c.c. of water. The aqueous extract is transferred to a 100 c.c. flask and evaporated nearly to dryness. The charred residue is ignited, the ash is moistened with 2 c.c. of strong sulphuric acid, and the mixture warmed; when the greater part of the hydrogen chloride has been expelled, the residue is added to the concentrated liquid in the distilling flask. The last portions are washed into the flask with 10 c.c. of methyl alcohol and the liquid is distilled nearly to dryness. Successive quantities of 10 c.c. of methyl alcohol are added to the cold residue, the distillation being repeated after each addition; six such treatments are usually sufficient to ensure the volatilisation of the whole of the boric acid. The alcoholic distillate is passed into 25 c.c. of water in a flask. When the distillation is finished, the liquid is evaporated until free from alcohol; the methyl borate is hydrolysed by this treatment and a solution of boric acid remains. This solution is diluted with a little water and rendered neutral to methyl-orange. An equal volume of glycerol is added, and the liquid is titrated with sodium hydroxide in presence of phenolphthalein just as in the preceding method.

The results of the estimation of boric acid in various samples of apples, pears, quinces, pomegranates, grapes, cider, and apple juice are appended. E. G.

Analysis of Coal. HENRI PELLET (*Chem. Centr.*, 1904, ii, 791—792; from *Bull. Assoc. Chim. Sucr. Dist.*, 21, 1203—1223).—Most of the ordinary methods of analysis of fuels are described and compared in the original paper, with special reference to the sugar industry. The samples of coal should pass through an 80 or 100 sieve. The moisture is determined by heating 1—2 grams at 100—105° and weighing for the first time in 10—15 minutes;

weights varying by 2 mg. or less are considered constant. The ash is estimated by gradually heating 0.5—1 gram in a flat platinum dish to a red heat in a muffle; under favourable conditions, the weight is constant in 15—30 minutes. The volatile matter is determined by heating 1—2 grams in a covered platinum crucible at a red heat; the crucible is heated for 3 minutes after gas has ceased to burn at the lid. The sulphur is estimated from the sulphuric acid formed in combustion in a calorimetric bomb, or by heating 1 gram of powdered coal with a mixture of 20 grams of sodium carbonate and 10 of potassium nitrate, and precipitating as barium sulphate. If iron sulphide is present in coal, it is converted on burning into ferric oxide and sulphuric acid, and the quantity of sulphate in the coal is not increased. Calcium carbonate is decomposed at a dark red heat in presence of silica.

Heraeus' electric furnace is recommended for the determination of the ash and volatile matters at 1000°, and for other operations which require a constant temperature. E. W. W.

Estimation of Carbon and Sulphur in Iron and Steel. A. MÜLLER (*Chem. Zeit.*, 1904, 8, 795—796; *Zeit. angew. Chem.*, 1904, 17, 1453—1454).—A compact form of apparatus is described for the combustion of the evolved gases. The whole is mounted on one stand and consists of a capillary platinum U-tube for the actual combustion, a drying tube, and a soda-lime absorption tube. The drying tube is a combination of a spiral and a U-tube. The spiral contains a mixture of phosphoric and sulphuric acids, whilst the limb of the U-tube next the combustion tube is filled with phosphoric oxide held in position by wads of glass-wool. The evolution flask is provided with a condenser reaching down the inside of its neck, the outlet for the gases being at the upper part of the neck (Corleis' pattern). In the estimation of sulphur, the platinum combustion tube is replaced by a quartz-glass tube and the hydrogen sulphide is absorbed by means of cadmium acetate. W. P. S.

An Improved Geissler Apparatus for the Estimation of Carbon Dioxide. ENGELBERT KETTLER (*Zeit. angew. Chem.*, 1904, 17, 1097—1098).—The apparatus described is a modified form of Schrötter's for the estimation of carbon dioxide in carbonates. It is provided with four openings; the first, for the tube containing the dilute acid; the second, for the introduction of the carbonate; the third is kept stoppered until the carbon dioxide evolved is practically all expelled from the apparatus, when a calcium chloride tube is attached to this opening and the removal of carbon dioxide then completed; the fourth contains the sulphuric acid for drying. The apparatus yields good results. A. McK.

Analysis of Soluble Glass (Sodium Silicate). PAUL HEERMANN (*Chem. Zeit.*, 1904, 28, 879—880, 883—884).—A paper dealing principally with the estimation of free alkali in commercial sodium silicate solution.

Ten grams of the sample are diluted with 100 c.c of water and mixed with 100 c.c. *N*-barium chloride. The mixture is diluted to 250 c.c.

and at once passed through a dry filter ; the first 20—30 c.c. are rejected. One hundred c.c. of the filtrate are now titrated with $N/10$ hydrochloric acid, using phenolphthalein as indicator.

L. DE K.

Gravimetric Estimation of Calcium. ENGELBERT KETTLER (*Zeit. angew. Chem.*, 1904, 17, 1488—1489. Compare this vol., ii, 517).—A reply to Brück (this vol., ii, 681). The author still thinks that weighing the calcium as sulphate is more convenient than its conversion into carbonate.

L. DE K.

Results obtained in Electrochemical Analysis by the use of a Mercury Cathode. RALPH E. MYERS (*J. Amer. Chem. Soc.*, 1904, 26, 1124—1135).—A lengthy paper unsuitable for adequate abstraction, setting forth the advantages of the use of a mercury cathode in the electrolytic separation of a number of metals. By its means even chromium may be quantitatively separated from aluminium.

L. DE K.

Volumetric Estimation of Lead. ERIC JOHN ERICSON (*J. Amer. Chem. Soc.*, 1904, 26, 1135—1139).—A modification of Walters and Affelder's method (*Abstr.*, 1903, ii, 614) applied to brasses and bronzes. The alloy is dissolved in nitric acid, and to the filtrate is added excess of ammonia and then some ammonium persulphate. On boiling, the lead is precipitated as dioxide and washed first with dilute ammonia and then with hot water. The precipitate is treated with nitric acid and a known volume of hydrogen peroxide, the excess of which is then estimated with standard permanganate solution. From the result, the amount of lead is readily calculated. The permanganate should preferably be checked against lead nitrate.

L. DE K.

New Method for the Volumetric Estimation of Copper, and its Application to the Testing of Copper Sulphate and Commercial Copper Sulphide. GIOACHINO GRIGGI (*Chem. Centr.*, 1904, ii, 367 ; from *Boll. Chim. Farm.*, 43, 392—394).—The reaction on which the method is based is the reduction of copper sulphate by hydroxylamine, according to the equation: $(\text{NH}_2\cdot\text{OH})_2\cdot 2\text{HCl} + 4\text{CuSO}_4 + 10\text{KOH} = 2\text{Cu}_2\text{O} + \text{N}_2\text{O} + 2\text{KCl} + 4\text{K}_2\text{SO}_4 + 9\text{H}_2\text{O}$. To a solution of 1.39 grams of hydroxylamine hydrochloride in water, 5.6 grams of potassium hydroxide are added, and the solution is made up to 1 litre. This hydroxylamine solution is then added gradually to the copper salt solution until reduction is complete ; heat may be required. The sulphates of iron, zinc, sodium, magnesium, and other metals interfere with the straightforward course of the reaction. J. C. P.

Electrolytic Assay of Copper containing Arsenic, Antimony, Selenium, and Tellurium. GEORGE L. HEATH (*J. Amer. Chem. Soc.*, 1904, 26, 1120—1124).—If the metal contains arsenic and antimony, but less than 0.01 per cent. of joint nickel, cobalt, and zinc, it is dissolved in nitric acid, evaporated with sulphuric acid, and finally

deposited electrolytically from an ammoniacal solution. For details of the electrolysis, the original paper should be consulted. If only traces of antimony, and less than 0.02 per cent. of arsenic, but large amounts of tellurium or selenium are present, the latter are removed by treating the boiling solution of the sulphate with a current of sulphur dioxide; the filtrate is then electrolysed. If the sample contains more than 0.01 per cent. of antimony and other elements, these may be removed by precipitation with ammonia in the presence of ferric nitrate.

The author has also introduced another process which is based on the fact that under certain conditions the electrolytic co-precipitation of any arsenic present is prevented by addition of solid ammonium nitrate.

L. DE K.

Analysis of Bauxite. TAUREL (*Ann. Chim. anal.*, 1904, 9, 323—327).—An aliquot part of the solution, free from silica, obtained by the usual process, is precipitated with ammonia, and, after purifying the washed precipitate, by redissolving in hydrochloric acid and reprecipitating with ammonia; it is finally ignited and weighed. It represents aluminium and ferric oxides, and possibly also titanitic acid. Another portion is then neutralised with ammonia, any precipitate is redissolved in formic acid, and some 5 c.c. of this is added in excess. After reducing the iron by means of a current of sulphur dioxide, the whole is boiled for an hour, and an excess of solution of ammonium citrate is added, followed by ammonia and ammonium sulphide. The precipitate so obtained, after washing and ignition, represents iron oxide and titanitic acid.

If it is desired to weigh the titanitic acid separately, an aliquot part of the solution is precipitated with ammonia, some 10 c.c. in excess of formic acid are added, the iron oxide is reduced completely with sulphurous acid, and the whole is very gently boiled for an hour. The precipitate is allowed to settle for a few hours, and the supernatant liquid is, so far as possible, siphoned off. The precipitate is then collected on a filter and washed with boiling water (it generally runs through the filter at first). It is finally ignited and weighed.

The filtrate may, of course, be used for a repeated iron determination.

L. DE K.

Electrolytic Estimation of Manganese. J. KÖSTER (*Zeit. Elektrochem.*, 1904, 10, 553—554).—A platinum-iridium basin and a platinum anode making 600—700 revolutions per minute are used. The solution contains 5 to 10 grams of ammonium acetate, 3 grams of chrome alum, and a few c.c. of alcohol in addition to the manganese salt, which must not be the chloride. A current of 0.04 to 0.045 ampere per sq. cm. may be used, which requires about 7 volts. The liquid is heated to 75° before beginning the electrolysis; the temperature should not be allowed to rise above 85°. Alcohol (about 10 c.c.) may be used instead of the chrome alum with almost equally good results. The quantity of manganese present should not exceed 0.3 gram, otherwise the precipitate is apt to peel off. The precipitation is complete in 20 to 25 minutes.

T. E.

Quantitative Precipitations and Separations by means of Ozone. PAUL JANNASCH and WILLY GOTTSCHALK (*Ber.*, 1904, 37, 3111).—On passing ozonised oxygen through a solution of manganese ammonium sulphate acidified with acetic acid, the manganese is quantitatively precipitated as manganese tetroxide. W. A. D.

Estimation of Manganese in Drinking Water. GEORG BAUMERT and PAUL HOLDEFLEISS (*Zeit. Nahr. Genussm.*, 1904, 8, 177—181).—From 250 to 1000 c.c. of the water, according to the amount of manganese present, are acidified with 1 c.c. of hydrochloric acid and evaporated to a volume of less than 100 c.c. Towards the end of the evaporation, a little zinc oxide or barium carbonate is added to precipitate any iron present. The whole is then filtered and the precipitate washed until the filtrate amounts to 100 c.c. Five c.c. of a 10 per cent. solution of sodium hydroxide are added to the latter, which should be contained in a stoppered flask, and the mixture shaken for 5 minutes, the stopper being frequently lifted to admit air. Five c.c. of a 10 per cent. potassium iodide solution are now introduced, together with sufficient hydrochloric acid, drop by drop, to dissolve the brown precipitate. After the addition of starch solution, the liberated iodine is titrated with sodium thiosulphate solution (about 0.3 gram per litre) which has been standardised against a solution of pure manganous chloride.

To avoid the evaporation of a large volume of the water, the manganese may be separated by Knorre's method (*Abstr.*, 1903, ii, 760) and then estimated by the above method. W. P. S.

Chemico-toxicological Detection of Potassium Permanganate. DIOSCORIDE VITALI (*Chem. Centr.*, 1904, ii, 794—795; from *Boll. Chim. Farm.*, 43, 493—504).—When potassium permanganate is taken into the organism, since no free acid is present except in the stomach, the hydroxide of manganese dioxide is formed. This change takes place so quickly that the administration of an antidote such as an acid solution of hydrogen peroxide is scarcely possible. When finely chopped meat is treated with the permanganate, the surface becomes brown; the presence of manganese can be detected in the ash by the violet coloration which is formed when it is treated with excess of concentrated sulphuric acid and potassium bromate added. The meat also gives the following reactions. By the action of concentrated hydrochloric acid, an intensely brown coloration is formed which becomes blue on the addition of water and potassium iodide. A similar coloration is also obtained by adding water and a few drops of guaiacum tincture. When the meat is treated with 10—20 times its quantity of concentrated hydrochloric acid and aloin then added, a red coloration is formed. A violet colour is obtained by adding water, an ethereal solution of phthalin, hydrochloric acid, and finally potassium hydroxide until alkaline, and shaking. By agitating the meat with dilute hydrochloric acid and some drops of a solution of aniline sulphate, a blue or bluish-green coloration is formed.

The hydroxide of manganese dioxide acts on the albumin, forming an albuminate. Since the permanganate only attacks the external

portions of the tissue, putrefaction of the internal portion is not prevented, and the ammonium sulphide which is formed reduces the manganese dioxide to oxide, and finally converts it into sulphide, the brown colour being of course destroyed; in such cases, a test for manganese can only be applied. Pugliese has found that in the case of guinea-pigs a dose of about 0.2 gram, and for men about 10 grams, of permanganate per kilogram is fatal. A tissue which has been treated with potassium permanganate decomposes hydrogen peroxide with great rapidity, liberating oxygen; the fibrin of blood has also this property, but to a much less degree.

E. W. W.

New Reaction for Iron in Copper. ED. CROUZEL (*J. Pharm. Chim.*, 1904, [vi], 20, 203—205).—Equal volumes of ten per cent. solutions of copper sulphate and sodium thiosulphate are mixed, when, after twenty-four hours, a greenish-yellow precipitate, passing into the yellow, crystalline double cuprous sodium thiosulphate, is formed, but if iron is present the colour is altered by the formation of an ochre-coloured basic ferric sulphate.

Should an excess of thiosulphate have been employed, the iron can be detected by means of potassium ferrocyanide.

G. D. L.

Estimation of Tungsten. LOYS DESVERGNES (*Ann. Chim. anal.*, 1904, 9, 321—323).—A criticism of various methods already proposed. The following method is said to give fairly correct results. Twenty-five c.c. of the alkali tungstate, obtained in due course, are neutralised with dilute nitric acid, using litmus solution as indicator; while boiling, a solution of mercurous nitrate containing precipitated mercuric oxide in suspension is added, and the mercurous tungstate so obtained, after being washed on a filter with a weak solution of mercurous nitrate, is dried and ignited. The residue consists of tungstic acid, which is then weighed as such. It is as well to repeat the analysis once or twice.

L. DE K.

Estimation of Uranium. F. GIOLITTI (*Gazzetta*, 1904, 34, ii, 166—170).—In a solution containing uranium in the form UX_4 , the addition of a slight excess of hydrofluoric acid causes the formation of a heavy, pulverulent, green precipitate, which is possibly UF_4 ; this can be readily washed both by decantation and on the filter with water rendered faintly acid with hydrofluoric acid. If the uranium is present in the liquid as a uranyl salt of the type UX_6 , it is necessary to reduce it to the form UX_4 before precipitating with hydrofluoric acid. On igniting the precipitate, together with the filter, at a bright red heat in an open crucible, it becomes completely converted into the oxide U_3O_8 , which can be weighed. If this oxide is further ignited in a current of dry hydrogen until it becomes constant in weight, it is reduced to the dioxide UO_2 , the weight of which acts as a check on that of the U_3O_8 . This method is given by the author for the estimation of uranium, and is found to yield good results.

Another, and in some ways more convenient, method of procedure with uranyl salts is to place the solution, together with 4—5 c.c. of concentrated hydrofluoric acid, in a smooth Classen electrolytic

capsule, the volume of liquid being then made up to 100—150 c.c. with water. Making the capsule the negative electrode and using a current density of about 0.8 ampere per sq. cm., the green, insoluble fluoride becomes loosely deposited on the capsule, from which it can be readily transferred to the filter. The ignition is then carried on as before. This method, in which the reduction is carried out without the introduction into the solution of foreign substances such as stannous chloride, also gives satisfactory results. T. H. P.

Estimation of Tin, Antimony, and [Arsenic] in Ores and Alloys. HENRI ANGENOT (*Zeit. angew. Chem.*, 1904, 17, 1274—1275).—The process is based on the use of sodium peroxide. On heating about half a gram of an ore or alloy containing tin, antimony, and perhaps arsenic and other metals, with 7 grams of sodium peroxide in an iron crucible, the three metals are rapidly oxidised and converted into sodium salts, which are then treated with water [or in the case of antimony with dilute alcohol (1:2)] and diluted to 250 c.c. The solution contains the tin and in some cases also arsenic or lead. On adding dilute sulphuric acid to 200 c.c. of the filtrate, the tin is precipitated as metastannic acid, and may be freed from any lead by heating with nitric acid; from arsenic, it may be freed by the ammonium chloride method (*Zeit. anal. Chem.*, 1895, 34, 557).

The antimony which is left undissolved as sodium pyroantimoniate is separated from any other insoluble metallic oxides by digesting in hydrochloric and tartaric acids, then treating the solution with sodium hydroxide and sodium sulphide. After filtering off any undissolved sulphides, the antimony is recovered by precipitation with dilute sulphuric acid, or the solution is submitted to electrolysis and the antimony weighed as metal. L. DE K.

Comparative Experiments on the Gravimetric Estimation of Antimony as Trisulphide and Tetroxide respectively. ALEXANDER GUTBIER and G. BRUNNER (*Zeit. angew. Chem.*, 1904, 17, 1137—1143).—Quite as good results can be obtained when antimony is estimated as tetroxide as when it is estimated as trisulphide, if the manipulation in the former case is conducted according to Brunck's method (*Abstr.*, 1895, ii, 372). A. McK.

Coloration of Borax Beads by Colloidal Dissolved Noble Metals. JULIUS DONAU (*Monatsh.*, 1904, 25, 913—918. Compare this vol., ii, 684).—If a borax bead is moistened with a solution of a gold salt and then fused, it becomes ruby-coloured, on long heating, blue and finally colourless unless much gold is present, when, after long heating, the bead is liver-coloured by reflected, blue by transmitted light. A solution containing 0.7 mg. of gold per 30 c.c. colours the bead red. The ruby colour is replaced by violet, and the reaction is less delicate if much sodium chloride is present. The reaction does not take place in presence of free sulphuric acid or halogens. The gold reaction is masked by the presence of more than 6 per cent. of platinum.

The borax bead is coloured yellow by silver. The reaction will

detect 0.00018 mg. of silver. The influence of other substances is the same as in the case of gold.

Platinum colours the borax bead reddish-brown by transmitted light; the reaction detects 0.00005 mg. of platinum, Iridium and osmium give coloured borax beads similar to the platinum bead. Rhodium gives a brown, and palladium and ruthenium black beads. G. Y.

Action of Soap on Calcium and Magnesium Solutions. V. HUGO GOTTSCHALK and H. A. ROESLER (*J. Amer. Chem. Soc.*, 1904, 26, 851—856).—A paper illustrated by curves showing peculiarities in the titration of calcium and magnesium salts with soap solution.

L. DE K.

New Method for destroying Organic Matter in Toxicological Analyses. ORESTE GASPARINI (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 94—100).—The author's method for destroying organic matter is as follows. The substance, after being freed as far as possible from alcohol, is covered with concentrated nitric acid in a beaker over which is placed a clock-glass provided with holes for admitting two glass tubes containing platinum wires connected with platinum electrodes. After the acid has been allowed to act for some time, a current of 4—6 amperes at a voltage of 8 is passed through the solution. The organic matter is destroyed either in a few hours or in a few days, according to the nature and quantity present and to the current intensity. In this way, the nitric acid is split up into ions, the hydrogen ion then acting on more nitric acid, forming water and nitrous acid, which latter then becomes resolved into water, nitric oxide, and nitrogen peroxide. The anion also probably reacts, thus: $2\text{NO}_3' + \text{H}_2\text{O} = \text{HNO}_3 + \text{O}$ and $\text{NO}_3' = \text{NO}_2 + \text{O}$. The nitrogen oxides and the nascent oxygen formed in this way readily oxidise the proteid substances. The solution is then filtered in the cold and the filtrate and wash-water evaporated as far as possible on the water-bath, the residue being then taken up in 35—50 c.c. of nitric acid and subjected once more to electrolysis for five or six hours. It is then evaporated to dryness, the residue dissolved in water, and analysed in the ordinary way. The insoluble portion, which may consist of fat, stannic oxide, antimonious oxide, silver chloride, and insoluble sulphates, is intimately mixed with a mixture of four parts of potassium nitrate with one of anhydrous sodium carbonate, and the whole gradually added to a porcelain crucible containing a little potassium nitrate. The mass is kept in a fused state for some time, then allowed to become nearly cold, and the crucible placed in a porcelain basin containing cold water. The remaining operations are conducted as usual.

With meat, eggs, &c., to which arsenic trioxide, mercuric chloride, silver, barium chloride, lead nitrate, zinc sulphate, or copper sulphate had been added, this method gave good results.

Sulphuric acid may be employed instead of nitric, but the oxidation is then slower and there is a tendency for the proteid substances to froth unpleasantly; further, some of the elements, arsenic for example, then give rise to volatile products.

T. H. P.

Estimation of Benzene Vapour in Coal-gas. OTTO PFEIFFER (*Chem. Zeit.*, 1904, 28, 884—885).—A half-litre separating funnel is filled with the sample of gas, and when all the air has been displaced, 2 c.c. of Harbeck and Lunge's reagent (equal vols. of sulphuric and fuming nitric acid) are introduced through the stem and left in contact with the gas for half an hour, the acid being allowed to spread over the sides of the funnel. Solution of sodium hydroxide is now introduced until the colour changes to orange-red, and hydrochloric acid is then added until the liquid just turns a pale sherry colour. The liquid is then shaken twice in succession with 50 c.c. of ether for 5 minutes, and the ethereal solution placed in a flask over 1 gram of dry potassium carbonate and 0.5 gram of blood charcoal. After a few hours, the liquid is filtered and the charcoal well washed with ether. The filtrate is heated in a flask on a water-bath until the ether has evaporated, and the residual dinitrobenzene is then dissolved in alcohol and estimated, volumetrically by Limpricht's process (*Abstr.*, 1878, 335), titrating with stannous chloride and iodine. L. DE K.

Contribution to the Analysis of Rose Oils. PAUL JEANCARD and C. SATIE (*Bull. Soc. chim.*, 1904, [iii], 31, 934—937).—The authors consider that the percentages of stearopten and of citronellol in rose oil are the most important criteria of its quality. The former is determined by dissolving 10 grams of the oil in 50 c.c. of acetone, cooling this mixture to -10° , and filtering through a tared paper placed in a well-cooled funnel. The stearopten so separated is dried over sulphuric acid under reduced pressure. The filtrate, which should not yield a further deposit when again cooled to -10° , is used, after the removal of the acetone by distillation, for the determination of citronellol and "total alcohols." The acid and saponification numbers are determined on the original oil. The paper gives tables of the principal constants of (1) oils distilled from Provence roses under various conditions, and (2) of the range of variation shown recently by Bulgarian rose oil. The results obtained with Provence oil are analogous to those found by Schimmel and Co. for Saxony oil.

T. A. H.

Estimation of Methyl Alcohol in Formaldehyde. HEINRICH BAMBERGER (*Zeit. angew. Chem.*, 1904, 17, 1246—1247).—When the sulphanilic acid method for estimating methyl alcohol in presence of formaldehyde according to Gnehm and Kaufler (this vol., ii, 520) is employed, a slight decomposition of the condensation product during the distillation cannot be avoided, and the slight amount of aldehyde which passes into the distillate appreciably influences the result.

The author's method is conducted as follows. The formaldehyde solution is mixed with sodium hydrogen sulphite and the condensation to sodium hydroxymethylenesulphonate conducted at the ordinary temperature for several hours in a closed vessel. The product is then exactly neutralised by sodium hydroxide and distilled; the amount of alcohol in the distillate is estimated by density determinations. Sodium hydroxymethylenesulphonate remains practically undecomposed when

heated in neutral solution. The results obtained by this method are higher than those obtained by Gnehm and Kaufler's method.

A. McK.

Two New Methods for the Estimation of Sugar. H. P. T. OERUM (*Zeit. anal. Chem.*, 1904, 43, 356—371).—(I) By the employment of Meissling's colorimeter (this vol., ii, 440) for the colorimetric estimation of the copper reduced by sugar from Fehling's solution, satisfactory results can be obtained. The cuprous oxide is collected on an asbestos filter (not on paper), and after washing is dissolved in 10 per cent. nitric acid and the colour compared with a standard solution of copper sulphate. As the amount of copper reduced is not strictly proportional to the sugar present, it is better to calculate the amount of the former from the colorimetric readings and to obtain the corresponding amount of sugar from a table such as Allihn's. The method has been found very serviceable for sugar estimations in urine.

(II) The mercury reduced by sugar from Sachsse's solution may be collected on a filter paper, washed first with warm 1 per cent. hydrochloric acid, and then thoroughly with water, dissolved in boiling nitric acid, and then titrated by *N*/10 ammonium thiocyanate with iron alum as indicator, exactly as in Volhard's method for silver estimation. It is well to standardise the solutions by a known amount of grape sugar. The rapidity and convenience of the method render it very suitable for clinical work.

M. J. S.

The Molisch-Udránszky α -Naphthol Sulphuric Acid Reaction. B. REINOLD (*Pflüger's Archiv*, 1904, 103, 581—617).—The best conditions under which this reaction can be obtained are described. By the gentle action of sulphuric acid on dextrose, no furfuraldehyde is formed, but another volatile compound, which gives a bluish-violet colour with α -naphthol and sulphuric acid; its spectrum shows an ill-defined band between λ 594 and 582. Besides this there are two other volatile substances formed, one of which is acid and the other neutral; the last gives the magenta-sulphuric acid reaction, but neither reduces ammoniacal silver solutions.

W. D. H.

Detection of Abrastol in Wine. EMILIO GABUTTI (*Chem. Centr.*, 1904, ii, 370; from *Staz. sper. agrar. ital.*, 37, 234—236).—The wine (100 c.c.) is treated with a few drops of ammonium hydroxide, extracted with amyl alcohol (10—15 c.c.), filtered, and evaporated to dryness. The residue is heated with some strong phosphoric acid, again heated after addition of 1—2 drops of a concentrated formaldehyde solution, and filtered. The filtrate shows a green fluorescence in presence of abrastol.

N. H. J. M.

Estimation of Cellulose in Foods and in Fæces. OSCAR SIMON and HANS LOHRISCH (*Zeit. physiol. Chem.*, 1904, 42, 55—58).—Ten grams of the substance (dried at 100°) are heated at 100° for 1 hour with 50 per cent. potassium hydroxide solution. When cold, 3—4 c.c. of hydrogen peroxide solution are added and, if necessary, the mixture is

again heated until it is colourless or only pale yellow. It is allowed to cool and then mixed with half its volume of 96 per cent. alcohol; if the solutions will not mix, a little concentrated acetic acid is added. The precipitated cellulose is allowed to settle, removed to a hardened filter paper, washed thoroughly with water, dilute acetic acid, alcohol, and ether. The precipitate usually contains a small amount of nitrogen (under 1 per cent.), and when obtained from fæces is extremely rich in ash (20—40 per cent.). J. J. S.

Estimation of the Total Acidity in Proteid Substances. SIRO GRIMALDI (*Chem. Centr.*, 1904, ii, 854—855; from *Staz. sper. agrar. ital.*, 37, 463—475).—It has been shown (*ibid.*, 35, 706) that the proteids, especially those of milk, combine with mineral acids to form compounds which are neutral towards the ordinary indicators. In order to determine the total acidity, an excess of normal sodium hydroxide solution is added to the milk which has been previously treated with a known quantity of sulphuric acid. The excess of alkali is titrated; the difference corresponds with the amount of acid added to the milk, and the natural acidity of the milk. A second method consists in determining the quantity of sulphuric acid which is necessary to cause coagulation of the milk on warming, adding normal sodium hydroxide solution until the coagulum is dissolved, and titrating the excess of alkali with decinormal sulphuric acid. The coagulum formed by rennet differs from that obtained by means of sulphuric acid in its behaviour towards dyes such as aromatic sulphonic acids. The methods described above are not, however, affected by the presence of organic acids. The results obtained are generally about twice as great as those found by the usual methods. E. W. W.

Toxicological Detection of Hydrogen Cyanide. DOMENICO GANASSINI (*Chem. Centr.*, 1904, ii, 718—791; from *Bull. soc. med.-chir. Pavia*. See this vol., ii, 758).

Estimation of Saturated Fatty Acids. WILHELM FAHRION (*Zeit. angew. Chem.*, 1904, 17, 1482—1488).—An adverse criticism of the new process introduced by Partheil and Férié (this vol., i, 5). L. DE K.

The Lithium Method of Separating Saturated Fatty Acids. K. FARNSTEINER (*Zeit. Nahr. Genussm.*, 1904, 8, 129—136).—Partheil and Férié have described a method for the separation of the saturated fatty acids of various fats and oils (this vol., i, 5), according to which 1 gram of the fat is saponified and precipitated from an alcoholic solution with lithium acetate. The solution is warmed to dissolve the precipitate, and, on cooling, lithium stearate, palmitate, and myristate (partially) are said to crystallise out, whilst lithium laurate and the remainder of the myristate remain in solution. The laurate is converted into the lead salt and separated, and the insoluble lithium salts separated by fractional crystallisation. The author has investigated this method, and comes to the conclusion that it is quite

untrustworthy, and that the percentages of palmitic, stearic, myristic, and lauric acids found by Partheil and Férié in butter, margarine, and lard are incorrect. Apart from the experimental data given, it is also shown that the presence of lauric and myristic acids in lard would considerably influence the saponification value of the latter. The lard examined by Partheil and Férié had a normal saponification value.
W. P. S.

Rapid Analysis of Cream of Tartar and Tartaric Acid Baking Powders. R. O. BROOKS (*J. Amer. Chem. Soc.*, 1904, 26, 813—818).—The total tartaric acid is estimated by Kenricks' polarimetric molybdate method (*Abstr.*, 1903, ii, 112). The amount of combined tartaric acid (as potassium hydrogen tartrate) is found by deducting the amount of carbon dioxide in the original powder from the quantity corresponding with the alkalinity of the white ash, and calculating the difference to its equivalent amount of potassium hydrogen tartrate. The difference between the total and combined tartaric acid then gives the free acid present.

Starch is best estimated by treating the powder with cold 3 per cent. hydrochloric acid. The undissolved starch is collected in a Gooch crucible, washed first with cold water, then with alcohol, and finally with ether. After drying at 110° for two hours, it is weighed, then ignited, and reweighed, when the loss will represent the starch.

L. DE K.

Rapid Method for Estimating Fat in Milk. J. VAN HAARST (*Zeit. angew. Chem.*, 1904, 17, 1212—1213).—Polemical. A reply to Siegfeld (*Abstr.*, 1903, ii, 458. Compare van Haarst, *Abstr.*, 1903, ii, 516).
A. McK.

Indirect Estimation of Milk Fat by means of Fleischmann's Formula. ALBERT STEINMANN (*Ann. Chim. anal.*, 1904, 9, 348—350).—A controversy with Pierre on the above subject.

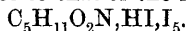
L. DE K.

Comparison of the Halogen Absorption of Oils by the Hübl, Wijs, Hanuš, and McIlhiney Methods. LUCIUS M. TOLMAN (*J. Amer. Chem. Soc.*, 1904, 26, 826—827. Compare *Abstr.*, 1903, ii, 458).—The original Hübl process is unsatisfactory. The process given by Hanuš (*Abstr.*, 1902, ii, 112) gives very good results provided the reagent is added from 60—70 per cent. in excess. Wijs's process (*Abstr.*, 1902, ii, 586) gives slightly higher results, but it is sufficient to add the reagent in excess to the extent of 35 per cent. In both these processes, 30 minutes' contact is sufficient to complete the reaction.

If it is desired to determine also the extent of the substitution, a solution of iodine chloride in carbon tetrachloride is recommended as being preferable to a solution of bromine in the same solvent (McIlhiney's reagent).
L. DE K.

Colour Reactions of Fatty Oils. Part III. HANS KREIS (*Chem. Zeit.*, 1904, 28, 956—957. Compare Abstr., 1903, ii, 114).—A *résumé* of the two earlier papers. Further particulars are given as to sesamol prepared by first agitating sesamé oil with hydrochloric acid and then so often with alcohol that the oil no longer gives the characteristic furfuraldehyde reaction. The alcoholic liquid is evaporated and the residue freed from fatty acids by treatment with dilute ammonia and calcium chloride. The filtrate then yields the sesamol to ether. It cannot be distilled without decomposition. In sulphuric acid, it dissolves with a green colour. Its ethereal solution, shaken with seed oils and nitric acid, gives a passing green coloration. The author thinks that sesamol is a phenol of high molecular weight with at least two hydroxyl groups in the meta-position and probably allied to naphtharesorcinol. If a piece of pine-wood is immersed in sesamol and then in hydrochloric acid of sp. gr. 1.19, it turns a dark green (a new lignin reaction).
L. DE K.

Betaine Periodide and the Estimation of Betaine by a Solution of Iodine in Potassium Iodide. VL. STANĚK (*Zeit. Zuckerind. Böhm.*, 1904, 28, 578—583).—The addition of a solution of iodine in potassium iodide solution to an aqueous solution of a betaine salt produces in the cold a brownish-red precipitate, rapidly changing into green crystals with metallic lustre, and in the hot to a green, metallic-looking oil which crystallises on cooling. The same precipitate is obtained by adding a solution of iodine in hydriodic acid to one of betaine or its hydrochloride. It is only slightly soluble in water, but on boiling with the latter, iodine is evolved and betaine hydriodide goes into solution; it is readily dissolved by alcohol, hydriodic acid, or aqueous potassium iodide. It melts at 58—61° with copious evolution of iodine vapours. Its composition varies with the conditions of formation and approximates to that of the hexa-iodide,



From very concentrated solutions of betaine, a solution of iodine in hydriodic acid precipitates a substance which has nearly the composition of betaine tri-iodide and which becomes green and assumes a metallic lustre when treated with water.

The betaine in a 1—3 per cent. solution of its hydrochloride is almost quantitatively precipitated by potassium tri-iodide (100 grams of potassium iodide and 153 grams of cyanogen-free iodine dissolved in 200 c.c. of water), when the solution is saturated with sodium chloride and the precipitate washed with saturated sodium chloride solution; the betaine in the precipitate is estimated by determining the nitrogen by Kjeldahl's method. When the betaine solution is very dilute or the precipitant is used in large excess, the results obtained are low. The betaine may also be precipitated from solutions containing 44 per cent. of sulphuric acid in place of the sodium chloride.

In this way, betaine may be separated from glycine, asparagine, tyrosine, glutamic acid, and ammonium salts. The precipitation is not affected by acetic or lactic acid, or by the constituents of the ash of molasses. Carbamide is partially precipitated with the betaine and a

marked precipitation occurs with the substances contained in Liebig's meat extract, probably peptones and purine bases.

In an acidified dilute solution of molasses, potassium tri-iodide produces a copious black, and to some extent crystalline, deposit containing 1.64 per cent. of nitrogen; 65 parts of this nitrogen consist of betaine-nitrogen. T. H. P.

Choline in Cerebrospinal Fluid. JULIUS DONATH (*Zeit. physiol. Chem.*, 1904, 42, 563—567).—Polemical against Mansfeld (this vol., ii, 623). The criticisms passed on the methods for detecting choline are shown to be fallacious. A combination of the author's method with that originally introduced by Halliburton and Mott excludes any possible confusion with inorganic chlorides, even although traces of the latter may be soluble in absolute alcohol. Various observers are quoted who have recently confirmed the value of the choline test. [No reference is, however, made to the results obtained by Allen (this vol., ii, 623) by the iodine test.] W. D. H.

Reactions for Brucine and Strychnine. I. Brucine. C. REICHARD (*Chem. Zeit.*, 1904, 28, 912—914).—If a solution of brucine or its sulphate is evaporated on the water-bath with addition of silver nitrate, the silver is partly reduced and a black powder remains covered with a varnish-like substance. If the latter is now moistened with a drop of solution of stannous chloride, a very characteristic deep red colour is obtained.

If a trace of brucine or its sulphate is triturated with a drop of a 10 per cent. formaldehyde and then evaporated to dryness, a residue is obtained which, on being moistened with a drop of stannous chloride, turns blue and changes to a yellowish-green on warming. L. DE K.

Estimation of Codeine in Opium. CHARLES E. CASPARI (*Pharm. Rev.*, 1904, 22, 348—352).—Fifty grams of opium are extracted with water and the aqueous extract evaporated on the water-bath to a volume of about 250 c.c. Five grams of barium acetate are added and the solution diluted to 700 c.c. The precipitate formed, consisting of the meconic acid and much of the resin, is collected on a filter and washed with cold water. The filtrate is again concentrated, treated with barium acetate, diluted, and filtered. These operations are repeated until the addition of barium acetate, followed by dilution, produces no further precipitate. The solution is then concentrated and a slight excess of 10 per cent. sodium hydroxide solution added. This precipitates the thebaine and narcotine, which are collected on a filter, the morphine, codeine, and narceine remaining in solution in the filtrate. The latter is acidified with dilute hydrochloric acid, concentrated, and an excess of 2 per cent. ammonia solution added. Most of the morphine is precipitated, and is collected on a filter and washed. The filtrate is again acidified, concentrated, treated with ammonia, and filtered if necessary. After acidifying and evaporating the filtrate to a volume of 75 c.c., it is rendered alkaline with ammonia and thoroughly extracted with benzene, which dissolves the codeine, but not the narceine. The

residue obtained on distilling off the benzene is treated with an excess of *N*/10 sulphuric acid, and the excess titrated with *N*/10 sodium hydroxide. A sample of Smyrna opium yielded 1.12 and 1.33 per cent. of codeine as the results of two estimations.

The author considers that there are two serious objections to Van der Wielen's method (Abstr., 1903, ii, 519). In the first place, the quantity of opium taken for the estimation is too small; and secondly, the use of an aliquot part of the ethereal solution does not conduce to accuracy.

W. P. S.

Estimation of Nicotine in presence of Pyridine. JAMES A. EMERY (*J. Amer. Chem. Soc.*, 1904, 26, 1113—1119).—The method is based on the fact that nicotine rotates the plane of polarisation, whilst pyridine does not. The liquid to be tested is compared polariscopically with a solution of pure nicotine of about 1 per cent. strength, which has been carefully checked against *N*/5 hydrochloric acid. The readings are expressed in degrees of the sugar scale. After deducting the alkalinity due to the nicotine from the total alkalinity, the amount of pyridine may be calculated with fair accuracy. In applying the process to the analysis of tobacco extracts, &c., the mixed bases are isolated by Kissling's process (extraction with ether in presence of sodium hydroxide, distillation of the ethereal residue, after adding some more alkali, in a current of steam, and titration with acid, using methyl-orange as indicator). If nicotine only is wanted, the tedious preliminary extraction with ether may be omitted.

L. DE K.

Alkaloid Reactions. C. REICHARD (*Chem. Centr.*, 1904, ii, 369; from *Pharm. Zeit.*, 49, 523—524. Compare Abstr., 1903, ii, 458, and this vol., ii, 374).—A trace of morphine, when added to a mixture of formaldoxime and concentrated sulphuric acid and heated, produces an intense bluish-violet, opaque liquid. The colour remains when a small amount of water is added, but dilution with much water almost decolorises the solution. Sodium hydroxide at once destroys the colour, ammonia less quickly.

Atropine when similarly treated, yields a brownish-black coloration, which disappears when a few drops of water are added. No coloration is produced with cocaine, strychnine, or brucine.

N. H. J. M.

Detection of Quinine by J. J. André's Reaction. P. GUIGUES (*J. Pharm. Chim.*, 1904, 20, [vi], 55—57).—The colour reaction of quinine with chlorine water and ammonia is prevented when tincture of orange is present.

G. D. L.

Some Colour Reactions. J. B. BALLANDIER (*J. Pharm. Chim.*, 1904, [vi], 20, 151—152).—On allowing bromine vapour to be absorbed by feebly acid solutions of quinine and quinidine, a pale yellow colour is produced. One drop of copper sulphate solution, followed by the gradual addition of ammonia, then gives a pink colour, changing to violet and finally green. Mineral acids, with the green solution, give blue or violet according to the acid used (the

green colour being restored by alkalis), the pink and violet solutions similarly yielding green colours with acids.

The green colour produced with quinine by bromine and ammonia is changed by copper sulphate to blue, which is unaltered by acids.

Chelidonine and narceine give the same green tint with sulphuric acid and the tannin of gall nuts, but chelidonine alone gives a pure carmine colour with sulphuric acid and guaiacol. G. D. L.

The Xanthine Bases in Meat, Yeast, and other Extracts.
II. In Yeast Extracts. KARL MICKO (*Zeit. Nahr. Genussm.*, 1904, 8, 225—237).—Methods are given for the further purification of the various fractions containing the xanthine bases of yeast extract (this vol., ii, 458), the processes being similar to those employed in the case of meat extract (*Abstr.*, 1902, ii, 369).

With regard to the occurrence of carnine in meat extracts, the author in no instance detected the presence of this base, and considers that it is either only occasionally present or that it is of a transitory nature.

Hypoxanthine was found to crystallise in two modifications. One form consisted of needles containing water of crystallisation, which spontaneously and readily lost their water, yielding anhydrous octahedra. W. P. S.

Chemical and Physiological Assay of Digitalis Tinctures.
GEORGE BARGER and W. VERNON SHAW (*Pharm. J.*, 1904, [iv], 19, 249—254).—A comparative study of the chemical and physiological methods of estimating the digitoxin in tincture of digitalis has shown that only the latter method is trustworthy. The amount of digitoxin found by Keller's method (*Abstr.*, 1898, ii, 267) is less than half the quantity actually present, and the digitoxin prepared in this way contains 33 per cent. of impurity. The results of the examination of several samples of digitalis tincture by both methods are tabulated. E. G.

Estimation of Tannin and Gallic Acid. W. PORTER DREAPER (*Chem. News*, 1904, 90, 111, 112).—For the method proposed, the following solutions are required: (1) copper sulphate solution of such strength that each c.c. corresponds with 0.05 gram of cupric oxide; (2) 50 grams of ammonium carbonate and 50 grams of sodium sulphite in 1 litre; and (3) 20 grams of lead acetate and 60 c.c. of glacial acetic acid in 1 litre. Fifty c.c. of the tannin solution, containing from 10 to 15 grams of the tannin material per litre, are titrated with the copper solution, after heating with excess of calcium carbonate and cooling. Potassium ferrocyanide is used as indicator. The result represents the total tannin and gallic acid expressed as cupric oxide. A second quantity of 50 c.c. of the tannin solution is then treated with 25 c.c. of the sulphite solution (2) and titrated with the copper solution. In this titration, the indicator must contain an excess of acetic acid. The result represents the tannin alone. The relation of cupric oxide to tannin may be ascertained by collecting the precipitate on a filter, drying at 105°, and weighing. The amount of copper

oxide present being known, the tannin may be calculated. Fifty c.c. of the tannin solution are again taken and treated with 10 c.c. of the lead acetate solution in the presence of barium sulphate. After shaking, the precipitate is collected on a dry filter and a small amount of anhydrous sodium sulphate added to the filtrate. The lead sulphate is filtered off and 40 c.c. of the filtrate heated with calcium carbonate and titrated with the copper solution. The result gives the gallic acid in the filtrate, and, by difference, the total tannin. The latter may or may not agree with the amount found in the second titration, any difference being due to the tannin (soluble or insoluble) in the ammoniacal solution. This classification of the tannins is a recognised one, and the method forms a means of quantitatively separating the two groups. W. P. S.

Volumetric Estimation of Methylene-blue. LOUIS PELET and V. GARUTI (*Bull. Soc. chim.*, 1904, [iii], 31, 1094—1097).—The authors, utilising the suggestion of Seyewetz (*Abstr.*, 1900, i, 356, 522, 614, 645) that the formation of insoluble compounds between basic and acidic dyes might be applied to the estimation of these substances, have carried out some experiments on the estimation of methylene-blue by means of crystalline ponceau, "carmine," pyramine-orange, and cotton-brown. Of these, the first is considered to give the best results.

To a known volume of the methylene-blue solution (0.5 per cent. in water) is added, drop by drop, a similar solution of the acid dye until a drop of the liquid placed on filter paper shows the tint of the acid dye used as a precipitant. The precipitate formed when crystalline ponceau is added to methylene-blue consists of 2 mols. of the former to 1 mol. of the latter; with "carmine," the compound produced contains 1 mol. of each dye. The pyramine-orange and cotton-brown used were impure and the composition of the precipitates formed with these was not determined. T. A. H.

Rapid Method of Distinguishing between Rosaniline and Pararosaniline. RUDOLF LAMBRECHT and HUGO WEIL (*Ber.*, 1904, 37, 3031).—If 1 part of commercial rosaniline is dissolved by heating with 20 parts of 30 per cent. hydrochloric acid, no crystallisation takes place on cooling, or even after some days. If pararosaniline is treated in the same way, the sparingly soluble hydrochloride crystallises out immediately the solution is cooled. This difference can be used to detect the presence of 0.5 per cent. of pararosaniline in rosaniline, the rust-coloured pararosaniline hydrochloride crystallising out after 12 hours; the presence of larger proportions of pararosaniline (5—10 per cent.) is shown by immediate crystallisation on cooling.

If rosaniline is dissolved in too small a volume of hydrochloric acid, the polyhydrochloride slowly separates in crystals. G. Y.

Estimation of Lecithin in Plants. ERNST SCHULZE (*Chem. Zeit.*, 1904, 28, 751, 752).—In the estimation of lecithin in plants and

seeds, the absolute alcohol used for the extraction does not dissolve out any phosphorus-containing compound other than lecithin. With regard to the decomposition of lecithin at temperatures exceeding 60°, the author considers that, for safety, this temperature should be adhered to. Whether the lecithin in combination with albumin is completely extracted at 60° still remains to be proved. The factor employed for calculating the phosphorus found into lecithin is only approximate, as lecithin has been obtained from rye and barley corns containing only 2.2 to 2.3 per cent. of phosphorus, whilst the usually occurring distearyl-lecithin contains 3.84 per cent. of phosphorus.

W. P. S.

The Ferricyanide Method of Estimating Oxygen in Blood. FRANZ MÜLLER (*Pflüger's Archiv*, 1904, 103, 541—580).—Some modifications of the Haldane-Barcroft apparatus are proposed, and the method is found to be highly satisfactory. Some investigations on the dissociation curve of dog's blood are described, and a number of researches on the question in health and disease are propounded for future work.

W. D. H.

Estimation of the Alkalinity of Blood. SERGEI SALASKIN and Z. PUPKIN (*Zeit. physiol. Chem.*, 1904, 42, 195—199).—Further experiments by the Salkowski-Salaskin method have been carried out. The process consists in heating the blood with ammonium sulphate under reduced pressure and in a Nencki-Zaleski apparatus, the temperature of the water-bath being kept at 40°. The operation lasts two hours. Good results can be obtained with 10 c.c. of blood. The values are quite different when water is added.

Under similar conditions, namely, reduced pressure at 40° and evaporation to dryness, sodium hydroxide, carbonate, and hydrogen carbonate evolve the equivalent amount of ammonia. In a 15 per cent. solution, disodium hydrogen phosphate drives out ammonia until it is half transformed into monosodium salt. The monosodium phosphate does not evolve ammonia. Similarly, proteids evolve practically no ammonia.

J. J. S.

Simple Clinical Method of Estimating the Different Proteids in Urine. ADOLF OSWALD (*Chem. Centr.*, 1904, ii, 858—859; from *Münch. med. Woch.*, 51, 1514—1515).—The amount of the different proteids in urine may be estimated by means of Esbach albuminometers in the following way. In the first, the total quantity of albuminous substances is estimated by means of Esbach's reagent. Three more are filled with urine from a burette to the mark U. To the second is added a quantity of a saturated solution of ammonium sulphate, sufficient to give a ratio of salt to urine of 28:7.2; the concentration in the mixture corresponds with 28 per cent. saturation and is equal to the limit of precipitation of fibrinogen. The third is the euglobulin fraction and in this a ratio of 3.6:6.4 and a saturation of 36 per cent. are obtained, whilst in the fourth or ψ -globulin fraction the ratio is made 5:5 and

the saturation 50 per cent. After shaking, the albuminometers are allowed to remain for several hours. The clear liquid is then removed by a siphon or by filtration, and the precipitate dissolved in water to which, preferably, a little sodium carbonate has been added. The albumin is then estimated in each case by means of Esbach's reagent in the usual way, a few drops of acetic acid being added if sodium carbonate has been previously used. Albuminometer 2 gives the quantity of fibrinogen or fibrinoglobulin. The quantity of albumin found in the precipitate from 3, less that obtained from the precipitate in 2, is equal to the quantity of euglobulin, and, similarly, 4—3 corresponds with the ψ -globulin and 1—4 the albumin.

The following results, expressed in percentages, have been obtained in cases of nephritis :

| | Total albumin. | Fibrinogen. | Euglobulin. | ψ -Globulin. | Albumin. |
|----------------------------|-------------------|-------------|-------------|-------------------|----------|
| Acute Scarlet Nephritis... | 10 | 0 | 2.5 | 1.5 | 6 |
| Acute Nephritis (advanced) | 12 | 0 | 0 | 0.5 | 11.5 |
| Acute Nephritis | 5 | 0 | 0.25 | 1.25 | 3.5 |
| Chronic Nephritis | 4—8 | 0 | trace | 1—2 | 3—6 |

E. W. W.

Detection and Estimation of Albumin in Urines. H. BELLOCQ (*Ann. Chim. anal.*, 1904, 9, 384—385).—One hundred c.c. of the clear urine are mixed with one gram of calcium acetate, neutralised with ammonia, and thoroughly boiled with constant shaking until the froth rapidly disappears when the source of heat is removed. The precipitate is at once collected, and, without washing, introduced into a 40 c.c. tube, where it is treated with 3 c.c. of nitric acid. The phosphates and oxalates dissolve, and the urates are also gradually decomposed with effervescence, whilst the albumin is not dissolved. The tube is now filled with strong alcohol and shaken. Any turbidity or deposit shows the presence of albumin. If the amount is to be estimated, the precipitate is collected, washed with alcohol slightly acidified with nitric acid, and then dried at a very moderate heat.

L. DE K.

Volumetric Estimation of Humus in Soil by means of Potassium Permanganate. W. ISTSCHEREKOFF (*Chem. Centr.*, 1904, ii, 559 ; from *J. exper. Landw.*, 5, 55—66).—The ground soil is boiled for 40—50 minutes with titrated permanganate solution, sulphuric acid and water in a 250—300 c.c. flask, and titrated with oxalic acid. It is sometimes necessary to boil with an excess of oxalic acid, to dissolve the manganese peroxide, and to titrate back with permanganate. The results agree well with those obtained by Gustavson's method.

The humus may also be estimated by weighing the carbon dioxide produced.

N. H. J. M.

General and Physical Chemistry.

Fluorescence. FRIEDRICH KEHRMANN (*Ber.*, 1904, 37, 3581—3583. Compare Kauffmann and Beisswenger, *Abstr.*, 1903, i, 700; this vol., ii, 528).—The author draws attention to a former paper (*Abstr.*, 1901, i, 52) in which he demonstrated a connection between the fluorescence of certain substances and the nature of the solvent, similar to that found by Kauffmann and Beisswenger. The change of fluorescence is probably due to a change in the position of the ortho-quinonoid linkings. C. H. D.

Comparison of the Ionisation produced in Gases by Penetrating Röntgen and Radium Rays. A. S. EVE (*Phil. Mag.*, 1904, [vi], 8, 610—618).—The chief objection to the view that the γ -rays and Röntgen rays are identical in their nature has consisted in the divergent effects produced by the respective rays when ionising various gases and vapours. All three types of radium rays produce ionisation currents proportional to the densities of the gases through which the rays pass, a law which has not been found to be valid in the case of the Röntgen rays. It is now shown, however, that when more penetrating rays from a hard bulb are employed, the law applies even in the latter case, except for methyl iodide; it was found to be valid for air, hydrogen sulphide, sulphur dioxide, chloroform, and carbon tetrachloride.

The author also criticises Paschen's conclusions (this vol., ii, 461) as to the nature of the γ -rays of radium. J. C. P.

Comparison of the Röntgen Rays with the Radiations emitted from Radiotellurium. E. VILLARI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1904, [iii], 10, 159—160).—The radiations from a copper rod covered with radiotellurium have a less penetrating power than X-rays. They are stopped by glass or aluminium, 1 mm. or less in thickness, and are incapable of passing through a sheet of ordinary paper. They penetrate slightly an ordinary linen handkerchief, and to a greater extent a very thin bladder or sheet of parchment. The air blown from a bellows over a glass tube rubbed on the radiotellurium rapidly acquires the power of discharging an electroscope and loses it slowly. When the rod itself is placed near the knob of the electroscope, the latter is rapidly discharged, but the discharge is retarded or accelerated by blowing the active air away from or towards the electroscope.

Air rendered active by X-rays loses its discharging power to only a small extent when passed through a slightly electrified tube, but if the electrification of the tube is strong, the air ionised by the X-rays has to be passed for about 2 hours in order to discharge the tube. On the other hand, air ionised by the radiotellurium reduces a strongly electrified glass tube to a non-electrified condition in a few minutes.

If the discharging capacity of carbon dioxide submitted to the action

of the radiotellurium radiations is taken as 1, that for air is 3—5, that for illuminating gas 7—8, and that for hydrogen 20.

T. H. P.

Radioactivity. C. BONACINI (*Nuovo Cimento*, 1904, [v], 8, 125—130. Compare this vol., ii, 530).—The author has made attempts to compare the gradation of a photographic plate acted on by light with that of a plate subjected to the radiations of radioactive material. The latter itself cannot be employed as the source of light, since the light it emits is not homogeneous over its whole surface, thus differing from the radioactive emanations. The ordinary scale employed in sensitometry with reference to light is inapplicable to the emissions from radioactive matter, owing firstly to the great penetrating power of the radiations and also to the diffusion which they undergo when they come into contact with other substances. Preliminary experiments show that the gradations in the cases of light and radioactive emanations exhibit marked differences.

Experiments have also been made on the transformations undergone by active radiations on meeting solid substances, the results already obtained by Madame Curie, by Becquerel, and by Villard being in disagreement. The substance the diffusion of which was to be studied was placed behind and in direct contact with a sensitive plate, which was then exposed to active radiations. After development of the plate, the diffused rays manifest themselves as a reinforcement of the general opacity in the region of contact.

All the substances experimented with by the author become active towards a photographic plate when struck by active radiations. The greatest effects are exhibited by lead, platinum, and substances which fluoresce under the action of these radiations, for example, barium platinocyanide and uranyl ammonium fluoride. Other conditions being the same, the actions are here greater than with the X-rays. The action is to be attributed mainly to the deviable constituent (β -rays) of the emanations. The diffused portion also undergoes transformation, its penetrative power being diminished. Radioactive emanations are also changed when they are transmitted by solid substances.

T. H. P.

γ -Rays of Radium. FRIEDRICH PASCHEN (*Chem. Centr.*, 1904, ii, 1101—1102; from *Physik. Zeit.*, 5, 563—568).—The photographic image obtained by means of γ -rays is not in any way affected by causing the rays to traverse an electric or magnetic field of 30,000 C.G.S. units or by opposing an *E.M.F.* of 7000 volts and reversing the strongest magnetic field. The ratio e/m must therefore be less than 1000, whilst for β -rays it is equal to 10^7 . The shadows cast by two platinum wires placed one above the other in close proximity are displaced by less than 0.1 mm. in the direction corresponding with the negative charge. The secondary effects are almost entirely due to γ -rays. Since e/m is small and m is at least 40,000 times greater than in the case of β -rays, the energy of a γ -ray electron must be very great. Madame Curie found that the heat evolved by radium in an ice calorimeter was increased by about 4 per cent. when the radium

was enclosed in an envelope of lead 2 mm. thick. The walls of the calorimeter absorbed about as much heat as the lead. From these data, it has been calculated that the γ -rays emitted by 1 gram of pure radium per hour are capable of producing 28 cal. if absorbed by lead. When lead was not used, the heat evolved by 1 gram of radium per hour was found to be 98.5 cal. In order to obtain an exact comparison, a calorimeter coated with lead of an average thickness of 1.92 cm. and a precisely similar calorimeter, but without the lead, were immersed in the same vessel containing ice and water. Fifty mg. of radium bromide were used. The contraction in the lead-covered calorimeter was found to be equal to 90 mg. of mercury per hour, but in the other to only 47. The γ -rays emitted by 1 gram of radium are able, therefore, to produce 126 cal. per hour, and the heat evolved is increased 2.26 times when these rays are absorbed. The energy of the β -rays of 1 gram of radium is less than 1.7 cal. per hour. The energy of a γ -electron is more than 3200 times greater than that of the most rapid β -electron in Kaufmann's measurements.

E. W. W.

Slow Transformation Products of Radium. ERNEST RUTHERFORD (*Phil. Mag.*, 1904, [vi], 8, 636—650).—The active deposit derived from the radium emanation undergoes three further rapid transformations (see this vol., ii, 223, and Bakerian Lecture, 1904), and the three corresponding products are now termed radium *A*, radium *B*, and radium *C*. The change $A \rightarrow B$ is accompanied by α -rays alone, $B \rightarrow C$ is a rayless change, while the further change of *C* gives rise to α -, β -, and γ -rays.

When metallic plates are exposed to the action of radium emanation, a residual activity is obtained on the plates, comprising both α - and β -rays, the latter being present in all cases in a very unusual proportion. The equality of the activity and the identity of the radiation from each plate show that the residual activity is due to changes of some material deposit on the plates, and that it cannot be ascribed to an action of the intense radiations. Further, while the β -ray activity of the above-mentioned residue remains constant, the α -ray activity gradually increases as time goes on, showing that the two types of rays arise from different products. The author's experiments further show that these two kinds of matter are (1) a product giving out only β -rays, which is soluble in sulphuric acid, but non-volatile at 1000°, and which is not deposited on bismuth; (2) a product giving out only α -rays, which is soluble in sulphuric acid, volatile at 1000°, and is deposited from a solution on bismuth.

As indicated above, the α -ray activity increases if the β -ray product is present, but it is found to remain sensibly constant if removed from the β -ray product by the action of a bismuth plate. Hence the β -ray product (radium *D*) is the parent of the α -ray product (radium *E*). The theory of two such successive changes is worked out, and thence with the experimental data available, it is estimated that the time necessary for half-transformation is in the case of *D* about 40 years, in the case of *E* about 1 year. The amounts of *D* and *E* in an old sample of radium chloride were found to be in good agreement with the values deduced from other data. These products, radium *D* and

radium *E*, must be present in pitchblende, and the author regards it as possible that *D* is the same as Hoffmann's radiolead (compare Abstr., 1903, ii, 402), and as almost certain that *E* is the radioactive constituent in Marckwald's radiotellurium (Abstr., 1903, ii, 81, 733). The question also is considered whether radium *E* may not be identical with Madame Curie's polonium. The two substances have similar chemical properties, and although radium *E* appears to be less volatile, the author adopts the view that polonium contains the same radioactive constituent as radiotellurium, that is, the fifth disintegration product of radium.

The separation of radium *D* from pitchblende would be of scientific value, and experiments with this object are in progress. J. C. P.

Properties of Radium Salts. ORAZIO REBUFFAT (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1904, [iii], 10, 133—134).—On vigorously rubbing a glass rod with a woollen cloth and approaching the finger to the rod, sparks are given off visible in the dark. If the experiment is made in the neighbourhood of a radium salt, the rod appears luminous all along the line of contact of the rod and cloth during the time the rubbing is taking place; if the finger is now rubbed along the rod, a luminous streak appears along the latter. The same phenomenon occurs when the rod is replaced by an evacuated glass tube.

If a sealed tube containing a radium salt and furnished with a tap is connected with an exhausted tube and the tap then opened, the previously exhausted tube will become luminous when rubbed with a woollen cloth, even after the lapse of several days. T. H. P.

Emanium. FRIEDRICH GIESEL (*Ber.*, 1904, 37, 3963—3966).—The emanium of the author differs from Debierne's actinium in two points. The activity of the emanium induction sinks in 34.4 minutes to half its original value, whereas 40 minutes are required for the same effect with actinium. The three lines which characterise the author's preparation have not been found with actinium. The most marked of those lines has λ 4885.4, whilst the other lines have λ 5300 and λ 5909 respectively.

Debierne's original preparations contained active thorium, whilst the author's contained inactive lanthanum.

The emanation from emanium differs from that from radium, since it cannot be expelled by heating or dissolving the preparation. The increase of activity observed with emanium is ascribed to the formation of a solid, non-volatile substance.

An active emanium preparation, in the form of oxide, was dissolved in hydrochloric acid a year after its preparation, and the rare earths, together with emanium, were precipitated by ammonia and the filtrate evaporated. The product obtained from the filtrate, after the ammonium chloride had been removed by volatilisation, consisted chiefly of strontium chloride, and emitted β -rays and an emanation. When dissolved in water and filtered, the β -rays were still emitted and the solution was luminescent. When the strontium was precipitated as carbonate, the whole of the active substance was contained in the pre-

precipitate, the filtrate being inactive. When this precipitate was dissolved in hydrochloric acid and then electrolysed, a trace of a yellow deposit was formed at the cathode, which emitted α - and β -rays strongly, but no emanation could be detected. The platinum anode was also active, although no deposit could be seen on it; it caused a zinc sulphide screen to phosphoresce, although to a much less extent than did the cathode. After a day, the activity of both electrodes had practically vanished. Since the deposit on the cathode indicated the presence of a heavy metal, the solution containing strontium chloride was treated with hydrogen sulphide. A faint turbidity resulted, and the solution was filtered. Although nothing could be observed on the filter paper, the activity of the latter was very intense, and scarcely diminished in intensity after several weeks.

A. McK.

Electrical Conductivity of Sodium and Potassium Chlorides in Mixtures of Water and Ethyl Alcohol. BERNHARD SCHAPIRE (*Zeit. physikal. Chem.*, 1904, 49, 513—541. Compare Roth, Abstr., 1903, ii, 126).—The alcoholic mixtures used contained respectively 10, 20, 25, 30, and 40 per cent. by volume of alcohol in the case of sodium chloride, 20, 30, and 40 per cent. in the case of potassium chloride. The measurements were carried out at the temperature of 18°.

The addition of alcohol to water lowers the equivalent conductivity of both salts, but the lowering for 1 per cent. of alcohol is not so great for the later additions of alcohol as it is for the first additions. The experimental values of the conductivity are satisfactorily reproduced by Kohlrausch's formula, $(\Lambda_{\infty} - \Lambda)/\Lambda^p = c\eta^{\frac{1}{2}}$ (Abstr., 1901, ii, 221). In the case of sodium chloride, the value of p decreases from 10 per cent. alcohol, has a minimum for 25 per cent. alcohol, and thereafter increases; the variation of c with the percentage of alcohol is exactly the reverse. In the case of potassium chloride, p increases with the concentration of the alcohol up to 25 per cent., after which it falls off; the variation of c is again the reverse. For both chlorides, Λ_{∞} diminishes regularly as the alcohol concentration increases. For a given alcoholic mixture, the ratio $\Lambda_{H_2O}/\Lambda_{alc.}$ diminishes as the dilution increases, and is not constant even in the most dilute solutions investigated. The conclusion drawn from this is that the mobility of the ions and the degree of dissociation are both diminished by addition of alcohol. The temperature coefficient of conductivity increases markedly with increase of the alcohol concentration, and for a given alcoholic mixture increases slowly with diminishing concentration of the chloride.

Wakeman's formula (*Ann. Phys. Chem.*, 1893, ii, 49) is found to apply satisfactorily in all cases, and Arrhenius's formula (Abstr., 1892, 1038) is valid up to 10 per cent. alcoholic mixtures.

When Λ/Λ_{∞} is taken as a measure of the dissociation, it is found that of the three expressions for the dissociation constant, due respectively to Ostwald, Rudolphi, and van't Hoff, none gives satisfactory results. It appears also that the transport number for the cation increases regularly as the alcohol concentration increases.

J. C. P.

Electromotive Forces produced at the Surface of Animal Membranes on Contact with Various Electrolytes. GINO GALEOTTI (*Zeit. physikal. Chem.*, 1904, 49, 542—562. Compare Abstr., 1902, ii, 377).—The fresh skin of a frog is in general the source of a potential difference when in contact with various electrolytic solutions; if the membrane, however, is killed, the potential difference can no longer be detected. The magnitude and direction of the *E.M.F.* produced depend chiefly on the nature of the electrolytic solution with which the membrane is in contact. With potassium chloride, bromide, or iodide as electrolyte, no *E.M.F.* is produced, which shows that a frog's skin has no intrinsic bioelectric property. Planck's theory of the contact potential between dilute electrolytic solutions may be applied to the above phenomena, if it is assumed that the inner and outer layers are permeable in different degrees to the various kinds of ions. J. C. P.

Anodic Dissolution of Metals and their Passivity. OTTO SACKUR (*Zeit. Elektrochem.*, 1904, 10, 841—844).—Between any metal and any aqueous solution an equilibrium is supposed to be reached which in the case of a bivalent metal would be represented by the equation $\text{Me} + 2\text{H}^+ \rightleftharpoons \text{Me}^{++} + \text{H}_2$. A passive metal does not decompose water, and in that case the pressure of the hydrogen is less than one atmosphere. The metal cannot dissolve unless the hydrogen is removed. An increase in the concentration of the hydrogen ions in solution increases the pressure of the hydrogen in the equilibrium and may therefore enable it to be evolved in the gaseous condition. Hydrogen ions, therefore, always tend to diminish or destroy passivity. Among the anions, NO_3^- and ClO_3^- always induce passivity, Cl^- and Br^- destroy it, whilst SO_4^{--} , CN^- , CNS^- , $\text{C}_2\text{H}_3\text{O}_2^-$, and OH^- occupy an intermediate position. The ease with which Cl^- or Br^- combines with hydrogen explains their action; the very slow depolarising action of NO_3^- or ClO_3^- may be due either to the very small concentration of the hydrogen (this would explain the passivity of platinum in all circumstances), or to the small contact action of the metal on the combination of oxygen and hydrogen. As far as can be seen from the few data available, metals which exert a considerable catalytic effect on this reaction never become passive (copper and silver, for example).

These views, of course, only apply to cases in which the passivity is not due to a film of oxide (iron in fused sodium hydroxide, aluminium); they apply, for example, to zinc, which does not precipitate copper from cyanide solutions, or nickel or cadmium from their nitrates, or ferrous iron from its sulphate. T. E.

Theory of Amphoteric Electrolytes. GEORG BREDIG (*Ber.*, 1904, 37, 4140).—A claim for priority (compare Johnston, this vol., i, 984). E. F. A.

Transport Number of Sulphuric Acid. OLIN F. TOWER (*J. Amer. Chem. Soc.*, 1904, 26, 1039—1065).—The apparatus used in this investigation has been described previously (Abstr., 1901, ii, 143). A plate of cadmium was employed as the anode and a platinum spiral

as the cathode. The electrolysis was continued for two or three hours at a constant temperature, and the quantity of electricity was determined by means of a silver voltameter. The liquid was divided into five portions, one at the anode, one at the cathode, and three in the middle. The first portion was analysed by precipitating the sulphuric acid as barium sulphate, whilst the other four portions were titrated with potassium hydroxide solution. The experiments were made with N , $N/2$, $N/5$, $N/10$, $N/20$, and $N/50$ sulphuric acid at a temperature, in most cases, of 20° , but in some cases of 8° or 32° . The results are tabulated.

The accuracy of the determinations seems to increase as the concentration decreases to $N/20$, and then becomes less owing to disturbances caused by the manipulation of the solution and the flow of the current. The results obtained at a temperature of 20° show that the transport number first decreases with the concentration, and then increases especially between $N/10$ and $N/20$. No such increase is observed between the same concentrations at 8° and 32° , although an increase appears in these cases at $N/50$.

The transport numbers found at the different temperatures with the three most dilute solutions are sufficiently constant to indicate either that no HSO_4 ions exist beyond the $N/10$ concentration, or that some compensation takes place in the dissociation of ions possibly even more complex than HSO_4 . The average value of the results gives 178.8 as the transport number of sulphuric acid in dilute solution at 20° . The temperature coefficient was found to be 1.1.

These results are compared with those of previous investigators, and agree best with those of Bein (Abstr., 1898, ii, 553).

The values obtained by Jones and Douglas (Abstr., 1902, ii, 59)* for the equivalent conductivity of dissociated sulphuric acid are probably much too low. It is shown that the migration number of the HSO_4 ion at 18° is 70, the value which has been adopted by Kohlrausch. Combining this with the transport number of sulphuric acid, the equivalent conductivity of sulphuric acid at 18° is found to be 396, and the migration number of the H ion, 326 at the same temperature. Noyes and Sammet (Abstr., 1903, ii, 126) obtained the value 330 for the latter quantity from transference experiments with hydrochloric acid.

E. G.

Thermal Expansion of Dilute Solutions of Certain Hydroxides. By GEORGE A. CARSE (*Proc. Roy. Soc. Edin.*, 1904, 25, 281—291).—The hydroxides studied were those of sodium, barium, and strontium. When sodium hydroxide is dissolved in excess of water at 15° , contraction takes place, increasing until the concentration of the hydroxide is 6.07 per cent.; at that point the contraction has reached its maximum (0.0044 c.c. per gram of solution), and thereafter diminishes, passing into an expansion about the concentration 12 per cent. of hydroxide. At higher temperatures, the maximum contraction is less, and shifts in the direction of smaller hydroxide concentrations. All the barium hydroxide solutions examined exhibit a contraction, the character of which is not much affected by change of temperature.

Solutions of strontium hydroxide also exhibit a contraction which diminishes as the temperature of mixture rises.

Adopting the thermal expansion formula $V_t = V_{15}[1 + a(t - 15) + b(t - 15)^2 + c(t - 15)^3]$, the author has evaluated the constants a , b , and c from his experiments, and shows that the volume at any temperature between 15° and 20° may be correctly calculated to within 5 units in the fifth decimal place. The foregoing formula was also used for the calculation of the expansion coefficients $\alpha_t = 1/v_t \cdot dv_t/dt$. J. C. P.

Latent Heat of Mixing for Associating Solvents. JOHANNES J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 7, 174—177).—To obtain an expression for the latent heat of mixing of a substance with an associated solvent such as water, it is necessary to take into account the change in the degree of association of the solvent. It is calculated that for dilute solutions the change in the degree of association of the water molecules results in the absorption of 325 cal. when 1 gram-molecule of a non-electrolyte is dissolved and of 325 i cal. for each gram-molecule of an electrolyte. This quantity of heat must be subtracted from the experimentally determined heat absorption in order to obtain the pure heat of mixing. H. M. D.

Properties of Mixtures. Melting Points of some Mixtures of Sugars. HENRI GILLOT (*Bull. Acad. Roy. Belg.*, 1904, 834—854).—The author has constructed a series of curves showing the relationship between melting point and percentage composition for a number of mixtures containing mannitol, dulcitol, dextrose, sucrose, and lactose in pairs. The results show that the melting point of a mixture of any two of these substances is never exactly the mean of the melting points of the two constituents, and that the addition of minute quantities of one sugar to another lowers the melting point of the latter even when the substance added is of higher melting point. The forms of the curves obtained show that, in all the mixtures examined, with the exception of the sucrose—lactose and sucrose—dulcitol pairs, definite compounds are formed between the two constituents. The sucrose—dulcitol curve shows three branches which may be due to the formation of isomorphous mixtures (compare Le Chatelier, *Abstr.*, 1894, ii, 179 and 223). T. A. H.

Molecular Elevation of the Boiling Point of Mixtures of Volatile Liquids. CHARLES MARIE (*Compt. rend.*, 1904, 139, 595—597).—The author has determined the molecular elevation of the boiling point of mixtures of alcohol and water containing resorcinol, which is soluble in each constituent; or benzophenone, acetophenone, naphthylamine, or phenyl benzoate, which are only soluble in alcohol; or alanine or asparagine, which are only soluble in water; and finds that the experimental values do not agree with the theoretical values calculated from Nernst's formula (*Zeit. physikal. Chem.*, 1893, 11, 1). Mixtures of the first type give results which are higher than the theoretical; mixtures of the second type give the same value for the molecular elevation of the boiling point of alcohol and

water as for pure alcohol, whilst mixtures of the third type show a depression of the boiling point. M. A. W.

Heats of Combustion of some Organic Compounds. PAUL LEMOULT (*Compt. rend.*, 1904, 139, 633—635).—By means of a table the author shows the close agreement between the experimental values obtained by Fischer and Wrede (compare this vol., ii, 468) for the heats of combustion of 35 organic compounds, and the corresponding values calculated from his own formula (compare *Abstr.*, 1903, ii, 410; this vol., ii, 12, 310, 382, 605). M. A. W.

An Electrically Heated and Controlled Thermostat. R. H. MACUMBER and CHARLES G. L. WOLF (*J. Pathol. Bacteriol.*, 1904, 10, 105—110).—The thermostat described and figured gives excellent results. The temperature is maintained by electrical heating, and the regulator produces much more constant temperatures than in gas-heated apparatus. W. D. H.

Changes of Density caused by Passage through Draw-plates. GEORG W. A. KAHLBAUM (*J. Chim. phys.*, 1904, 2, 537—548).—It is impossible to give a definite value for the density of a metal; any value, however carefully determined, refers solely to the particular specimen employed. The author has determined the density of platinum wire before and after drawing through drawplates of diameters 0.7 mm. and 0.4 mm. The wire was at first 1 mm. in diameter. After its density had been determined, it was raised to a white heat for 3 minutes, allowed to cool, and the density again determined. It was then cold-drawn and the operations repeated. The six values so obtained for the density were, (1) 21.4136, (2) 21.4314, (3) 21.4181, (4) 21.4314, (5) 21.4142, (6) 21.4308. Two other specimens which at first had densities 21.4226 and 21.4233 ultimately gave values 21.4310 and 21.4317. These results show that, as indicated by previous observations, great compression produces a diminution of density, whilst heating then produces an increase of density; the values after this treatment seem to tend to a constant value. The experiments are being continued. L. M. J.

Viscosity of Liquid Mixtures. ALBERT E. DUNSTAN (*Zeit. physikal. Chem.*, 1904, 49, 590—596).—In continuation of work previously described (*Proc.*, 1903, 215; 1904, 117), mixtures of ethyl alcohol and carbon disulphide, ethyl alcohol and mercaptan, ethyl alcohol and acetone have been found to behave normally. The viscosity-concentration curve for ethyl alcohol and benzaldehyde resembles that for benzene and ethyl alcohol (*loc. cit.*) in exhibiting a minimum. Maxima are found to occur, not only for ethyl alcohol and water (*loc. cit.*), but also for (1) methyl alcohol and water and (2) acetic acid and water. J. C. P.

Viscosity of Solutions in relation to the Constitution of the Dissolved Substance. ARTHUR A. BLANCHARD (*J. Amer. Chem. Soc.*, 1904, 26, 1315—1339).—The relations between the velocity of

migration of various elementary ions and the viscosity of solutions of their salts have been studied by Wagner (*Abstr.*, 1890, 441) and Euler (*Zeit. physikal. Chem.*, 1898, 25, 239). Euler has found that in the alkali metal series, as the atomic weight decreases, the rate of migration of the ion also decreases, whilst the viscosity increases. To account for this, it is suggested that the lower the atomic weight of the alkali metal, the greater is the tendency of its ion to unite with the solvent.

The viscosity of solutions of ammonia and pyridine in water at 25° and of water in alcohol at the same temperature has been determined and the results are tabulated. In calculating the viscosity of these solutions the linear formula was employed, and a correction was applied for the amount of solvent displaced by the dissolved substance.

The viscosities were also determined of solutions of silver nitrate, copper nitrate and sulphate, and zinc sulphate and chloride to which varying amounts of ammonia had been added. When sufficient ammonia was present to form the soluble metal ammonium compounds, a large decrease in the viscosity was observed; on the further addition of ammonia, the increase in the viscosity was nearly the same as would have been produced by the addition of the same quantity of ammonia to pure water. The results of these experiments have been plotted as curves from the form of which the composition of the complex existing in the solution can be inferred. The decrease of viscosity on the addition of ammonia to solutions of metallic salts is compared with the negative viscosity of certain solutions, and it is shown that both are capable of explanation on the assumption that the ions exist in combination with a certain number of molecules of the solvent.

Viscosity measurements were made to determine the effect of additions of water to solutions of alkali hydroxides and cupric chloride in ethyl alcohol. The results, although affording no very definite conclusions, support the suggestion already mentioned that the ions of the alkali metals of lower atomic weight are more highly associated with molecules of the solvent. In the case of copper chloride, a maximum of increase in viscosity was observed corresponding with the minimum of conductivity found by Jones and Lindsay (*Abstr.*, 1903, ii, 55) and probably due to the same cause, namely, a maximum formation of highly associated molecules.

E. G.

Thickness of the Capillary Film between the Homogeneous Phases of Liquid and Vapour and its Relation to the Critical Phenomena. GERRIT BAKKER (*Zeit. physikal. Chem.*, 1904, 49, 609—617. Compare *Abstr.*, 1903, ii, 62).—The author's arguments lead to the view that the thickness of the capillary film becomes extremely great at temperatures just below the critical temperature. The temperature at which the meniscus vanishes is the temperature at which the capillary film has become too thick to permit the observation of a practically discontinuous refraction of the light.

J. C. P.

***Px* Curves of Mixtures of Acetone and Ethyl Ether and of Carbon Tetrachloride and Acetone at 0°.** G. C. GERRITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 7, 162—173).—The connection between the vapour tension, the molecular concentration of the vapour and that of the liquid mixture has been determined. The composition of the vapour phase is calculated from the refractivity measured by Rayleigh's method. In the case of the mixture of acetone and ethyl ether there appears to be a maximum pressure in the neighbourhood of pure ethyl ether. The curve representing the partial pressure of the ether is convex to the axis of concentration from 0—66 per cent. of ethyl ether; at this point the curve changes its direction, and is concave to the axis from 66 to 100 per cent. of ethyl ether. The acetone partial pressure curve is always concave to the concentration axis. The relative concentration of the ethyl ether is always greater in the vapour phase than in the liquid phase.

In the case of mixtures of carbon tetrachloride and acetone, both partial pressure curves are always concave to the axis of concentration, and the vapour phase is always richer relatively in acetone than the liquid phase.

H. M. D.

Derivation of the Formula which gives the Relation between the Concentration of Coexisting Phases for Binary Mixtures. JOHANNES D. VAN DER WAALS (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 7, 156—162).—A mathematical paper unsuitable for abstraction.

H. M. D.

Van der Waals's ψ -Surface. IX. The Conditions of Coexistence of Binary Mixtures of Normal Substances according to the Law of Corresponding States. H. KAMERLINGH ONNES and C. ZAKRZEWSKI (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 7, 222—233).—A theoretical paper unsuitable for abstraction.

H. M. D.

Determination of the Conditions of Coexistence of Vapour and Liquid Phases of Mixtures of Gases at Low Temperatures. H. KAMERLINGH ONNES and C. ZAKRZEWSKI (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 7, 233—244).—An apparatus is described for determining the composition of the coexisting phases by measurement of the pressure and volume at the beginning and end of condensation for binary mixtures of known composition. It seems probable that this method is to be preferred to the method of separating portions of the two phases and analysing these by chemical or physical means, for, as a rule, the analysis of a gaseous mixture cannot be so accurately performed as the preparation of a mixture of definite composition, and it is difficult to ensure the removal of fair samples of the two phases for the purposes of analysis. The commencement of condensation is determined by observation of a reflecting surface platinised by heating strongly with platonic chloride in camomile oil. The end condensation pressure is measured by replacing the dew-point apparatus by a piezometer.

H. M. D.

Small Ionic Concentrations. FRITZ HABER (*Zeit. Elektrochem.*, 1904, 10, 773—776).—Continuing the discussion on this subject (this vol., ii, 607 and 713), the author holds that it is not allowable to assume the law of mass action in solutions which are thousands of times more dilute than those for which the law has been proved experimentally.

If, for example, the lantern of a lighthouse were to revolve so slowly that a given place were illuminated once only in a night, that place could not be said to be light; similarly, if an ion only “flashes out” for a moment in a solution once a day, that ion cannot be considered to have a real concentration in the solution.

The tendency to assume that instantaneous reactions are due to extremely minute quantities of ions is probably due to a failure to realise the enormous reaction velocities involved by the assumption. The velocity of a reaction is given by the product of the velocity constant (velocity at unit concentration) and the concentration. If the latter is very small, the former must be very large in order that the product shall be large; by considering the reciprocal of the velocity constant (that is, time required for unit quantity of reaction) and assuming the usual atomic dimensions, it is possible to compare reaction velocities with well known physical quantities such as the velocity of electricity. In this way it was shown (this vol., ii, 607) that the assumption that small ionic concentrations are responsible for rapid reactions leads to velocities so large as to be almost inconceivable.

These difficulties are avoided by supposing that all molecules are capable of reacting, the class of molecules which contain electrons (ions) reacting more rapidly than the others on account of the great mobility of the electrons, just as the hydrogen compounds of organic radicles react more rapidly than their alkyl or phenyl compounds. Hence if ions are present in considerable quantity the reaction will be mainly ionic; if they are present in minute quantity or absent (as in Kahlenberg's experiments) the reactions will take place, on the whole, between undissociated molecules. In either case, the reaction may appear to be “instantaneous,” the means of observation not permitting degrees of rapidity in such cases to be distinguished.

T. E.

New Modes of Formation of Colloidal Solutions. Behaviour of the Latter towards Barium Sulphate. LUDWIG VANINO and F. HARTL (*Ber.*, 1904, 37, 3620—3623).—*Aspergillus oryzae* is a strong reducing agent, and is specially suited for the preparation of colloidal metals. A solution of gold chloride containing 0.01 gram in 100 c.c. of water, into which the mould was sown, assumed a blue colour after several days. The mould grows rapidly both in dilute and in concentrated solutions. Colloidal gold may also be obtained when an alcoholic solution of phosphorus is added to gold chloride.

Since Vanino has shown previously that the question as to whether the colour of a solution is due to a substance in solution or in suspen-

sion may be settled by shaking the solution with barium sulphate, the authors have examined the action of barium sulphate on various colloids, such as arsenic trisulphide, antimony sulphide, cadmium sulphide, copper sulphide, silver sulphide, and silver. Special precaution must be taken that the barium sulphate used is pure. Solutions of the cyanides of the heavy metals are particularly suitable for the preparation of colloidal sulphide solutions. The colloidal solutions examined were agitated with barium sulphate; since the filtered solutions were clear, the action of the barium sulphate was simply mechanical.

A colloidal gold solution is decolorised by long-continued shaking, during which various tints appear until all the gold is precipitated.

Colloidal solutions are regarded by the authors as containing solid particles in suspension.

A. McK.

Migration of Colloids. W. R. WHITNEY and J. C. BLAKE (*J. Amer. Chem. Soc.*, 1904, 26, 1339—1387).—The colloidal gold solutions used in the experiments described in this paper were prepared by the action of an ethereal solution of gold chloride on an aqueous solution of acetylene. Such solutions, even after prolonged dialysis with conductivity water, retain a constant conductivity five or six times as great as that of the water outside the dialyser.

Some of the solution was placed in a vertical tube closed at each end by means of goldbeaters' skin with which the electrodes were in contact. On passing the electric current, the gold migrated to the bottom, a colourless liquid being formed at the top and separated by an easily visible boundary from the coloured gold solution beneath. By observing the movements of this boundary, the rate of migration could be ascertained. The conductivity of the solutions is attributed to the presence of electrolytes associated with, or adsorbed by, the gold, since it is found that the conductivity is almost completely lost by repeatedly migrating the gold downwards on to the membrane of goldbeaters' skin and redissolving it in pure water.

The rate of migration has been determined for gold, platinum, silver, Prussian blue, ferric hydroxide, silicic acid, and gelatin. It has been found that the rate of migration of colloids is directly proportional to the potential gradient. In certain cases, a reverse effect takes place, consisting either in a sudden retardation of the downward movement of the boundary or in a reversal of its direction. The cause of this phenomenon is discussed.

For an account of the various experiments and the results obtained, the original must be consulted.

E. G.

Determination and Calculation of Equilibria for Highly Dissociated Acids. KARL DRUCKER (*Zeit. physikal. Chem.*, 1904, 49, 563—589. Compare Rothmund and Drucker, this vol., ii, 231).—From the dissociation constant obtained for picric acid (*loc. cit.*), the author deduces $\lambda_{\infty} = 342$, and hence $\mu_H = 312$ at 18°. When this value, which is lower than that usually accepted, is taken as the basis of λ_{∞} for bromoacetic, dichloroacetic, trichloroacetic, and $\alpha\alpha\beta$ -tri-

chlorobutyric acids, Ostwald's dilution law is satisfactorily fulfilled in some cases, but not in others.

An attempt has been made to determine the dissociation constants for strong or moderately strong acids by the aid of partition experiments, as for picric acid (see *loc. cit.*). In benzene, however, which has almost exclusively been used as the other liquid along with water, many acids are associated, and the necessity of determining the equilibrium between the simple and the complex molecules in benzene solution by freezing-point experiments somewhat diminishes the accuracy of the method. The equilibrium constants obtained are recorded in the following table: k is the dissociation constant of the acid in aqueous solution; x is the partition coefficient for the simple molecules between water and benzene (water and chloroform in the case of sulphurous acid); K is the association constant in benzene solution.

| | k . | x . | K . |
|--|---------|-------|-------|
| Trichloroacetic acid | 0.2—0.4 | 17.8 | 33 |
| Dichloroacetic acid | 0.0515 | 20.6 | 5? |
| $\alpha\alpha\beta$ -Trichlorobutyric acid ... | 0.180 | 0.62 | 6.9 |
| Sulphurous acid (1st stage)... | 0.016 | 0.70 | — |

From conductivity and partition experiments with mixtures of two acids (picric and iodic acids, bromoacetic and hydrochloric acids, dichloroacetic and trichloroacetic acids, dichloroacetic and trichlorobutyric acids, dichloroacetic and hydrochloric acids, picric and hydrochloric acids, trichloroacetic and hydrochloric acids), deviations from the dilution law could be detected in all cases at high concentrations, but only in one case with certainty when the concentration of each acid was less than 0.02 normal.

J. C. P.

The Function of Peroxydase in the Reaction between Hydrogen Peroxide and Hydriodic Acid. ALEXIS BACH (*Ber.*, 1904, 37, 3785—3800. Compare this vol., i, 542, 792).—The presence of oxydase from horse-radish roots increases the oxidising action of hydrogen peroxide on hydriodic acid. This increases, on the one hand, with the concentration of the peroxydase, on the other with the concentration of the hydrogen iodide up to a maximum, when the activity remains constant; and the conclusion is drawn that the three substances react with one another in definite proportions. For equal increases in activity, it has been found that the product of the concentrations of oxydase and hydrogen iodide is a constant, so that the activity of the peroxydase, that is, the ratio hydrogen peroxide | peroxydase is inversely proportional to the concentration of the peroxydase, but directly proportional to the concentration of the hydrogen iodide.

The increase in decomposition is also exactly proportional to the square root of the concentration of the hydrogen iodide. But with another specimen of peroxydase, it was found that, after the peroxydase maximum had been reached, the increase in the decomposition was directly proportional to the concentration of the hydrogen iodide.

It appears probable that different specimens of peroxydases contain

different amounts of at least two distinct catalysers. Any generalisations drawn with regard to any specimen of a ferment can only be regarded as holding good for that special specimen. Peroxydase is only slowly acted on by iodine or by hydrogen peroxide, but in the presence of the two it is comparatively readily destroyed. In order to obtain the best results from any peroxydase, a given concentration of hydrions is essential; this may be accomplished either by the presence of excess of hydriodic acid or by the addition of free acetic acid.

An increase of temperature from 16° to 38° diminishes the increase in activity to a considerable extent. J. J. S.

Isomerisation. MAURICE DELACRE (*Bull. Acad. Roy. Belg.*, 1904, 950—954. Compare Abstr., 1902, i, 79).—The author divides the phenomena of isomerisation into two groups: (1) in which the action is complete and non-reversible, the resulting product being quite distinct from the initial one, and (2) in which it is incomplete and reversible, as in the formation of pinacolin (*loc. cit.*). In the second group, the product may be a mixture of two substances in chemical equilibrium. The author states that there is only a superficial resemblance between this and tautomerism. Incidentally it is pointed out that so far little attention has been given to proving rigorously the individuality of isomerides. T. A. H.

New Laboratory Apparatus. RUDOLF L. STEINLEN (*Chem. Zeit.*, 1904, 28, 1051).—The glass valve previously described (this vol., ii, 722) is modified so that it can be used as a Bunsen valve, and, further, so as to serve as an automatic seal to a reduction flask.

L. DE K.

Inorganic Chemistry.

Influence of Indifferent Ions on the Electrolytic Formation of Periodic Acid and its Salts. ERICH MÜLLER (*Zeit. Elektrochem.*, 1904, 10, 753—756).—The influence of indifferent ions on the electrolytic oxidation of iodates to periodates in neutral solutions observed by the author (this vol., ii, 250) was difficult to follow quantitatively, owing to the simultaneous oxidation of the indifferent ions themselves. The author now observes that the presence of a fluoride increases the yield of periodate per ampere hour from almost nothing to about 30 per cent. of the theoretical quantity. It is found that the addition of hydrofluoric acid to a solution of iodic acid increases the difference of potential between the anode and a *N*/10 calomel electrode from about 1·8 volts to more than 2 volts. The influence of fluorine on anodic oxidation has already been observed by Skirrow (*Abstr.*, 1903, ii, 69). The author has previously shown that iodate is oxidised to periodate at a lead peroxide anode, but the potential is some 0·4 volt below that required to produce the same effect at a platinum anode in presence of a fluoride. He concludes that in one case the

reaction is brought about by decreasing the "chemical resistance," whilst in the other it is produced by increasing the anodic potential.

T. E.

Preparation of Persulphates. ERICH MÜLLER (*Zeit. Elektrochem.*, 1904, 10, 776—781).—The addition of hydrofluoric acid to a solution of potassium hydrogen sulphate very materially increases the yield of potassium persulphate which is obtainable by electrolysis (*Abstr.*, 1902, ii, 450). The yield, calculated from the quantities of oxygen and hydrogen evolved during the electrolysis, is increased from some 50 per cent. of the theoretical quantity to nearly 80 per cent. by the addition of hydrofluoric acid. Platinum electrodes are used, the current density being 0.2 ampere per sq. cm. at the anode and about 1 ampere per sq. cm. at the cathode.

With one anode, however, the addition of hydrofluoric acid had no effect, the persulphate crystals clinging to its surface instead of falling to the bottom of the vessel. The reason of this peculiarity was not discovered, although it appeared to be connected with the roughness of the surface; a very smooth surface appears to give the best result.

Measurements of the anode potential show that the addition of the hydrofluoric acid causes a sudden and considerable rise in its value; the increased production of persulphate is doubtless intimately connected with this rise.

T. E.

Density of Nitrogen Monoxide and the Atomic Weight of Nitrogen. PHILIPPE A. GUYE and ALEXANDRE PINTZA (*Compt. rend.*, 1904, 139, 677—679).—The authors have redetermined the density of nitrogen monoxide, using the method employed by Pintza and Jaquered (compare this vol., ii, 612), in the case of sulphur dioxide and oxygen, and obtain the value 1.97788 grams for the weight of a litre of the gas under normal conditions of temperature and pressure, a result which agrees closely with those obtained by Rayleigh (1.97745) and Leduc (1.97803). The atomic weight of nitrogen as calculated from this value by the method of density limits is 13.99, whereas the value 14.013 is obtained if the molecular weight of nitrogen monoxide is determined by comparing the densities of carbon dioxide and nitrogen monoxide under corresponding conditions, 12.005 being taken as the atomic weight of carbon. The results obtained by the authors and their colleagues for the atomic weight of nitrogen are summarised in the following table:

| Method. | Atomic weight of nitrogen. |
|---|-------------------------------|
| Density limits of nitrogen (compare Guye, this vol., ii, 475) | 14.004 |
| Gravimetric analysis of N ₂ O (compare Guye and Bogdan, this vol., ii, 557) | 14.007 |
| Volumetric analysis of N ₂ O (compare Jaquered and Bogdan, this vol., ii, 557) | 14.019 |
| Ratio of densities N ₂ O : CO ₂ (present paper) | 14.013 |

The discrepancy between the mean value ($N = 14.011$) and the value adopted by the International Commission for Atomic Weights in the table for 1904 ($N = 14.04$) calls for a revision of the latter value.

M. A. W.

Trithio-oxyarsenic Acid. LEROY W. McCAY and WILLIAM FOSTER (*Zeit. anorg. Chem.*, 1904, 41, 452—473. Compare this vol., ii, 253).—Sodium trithio-oxyarsenate, $\text{Na}_3\text{AsOS}_3 \cdot 11\text{H}_2\text{O}$, is unstable, being acted on by light at the ordinary temperature with the probable formation of the thioarsenate and the dithio-oxyarsenate. *Sodium strontium trithio-oxyarsenate*, $\text{NaSrAsOS}_3 \cdot 10\text{H}_2\text{O}$, prepared from strontium chloride and sodium trithio-oxyarsenate, forms white crystals which gradually become yellow. *Calcium trithio-oxyarsenate*, $\text{Ca}_3(\text{AsOS}_3)_2 \cdot 20\text{H}_2\text{O}$, forms unstable needles. A salt with the possible composition $\text{Ba}_7\text{Na}_2\text{As}_2\text{O}_7\text{S}_{14} \cdot 12\text{H}_2\text{O}$ is described. *Potassium trithio-oxyarsenate*, $\text{K}_3\text{AsOS}_3 \cdot 7\text{H}_2\text{O}$, prepared by the addition of potassium hydroxide to magnesium trithio-oxyarsenate, is a yellow oil which crystallises at -20° . *Potassium barium trithio-oxyarsenate*, $\text{KBaAsOS}_3 \cdot 7\text{H}_2\text{O}$, forms yellow crystals.

By the action of solutions of weak bases or of dilute solutions of strong bases on a large excess of antimony pentasulphide, considerable amounts of trithio-oxyarsenic acid are produced. A. McK.

Preparation of Silicon and its Chloride. ARNOLD F. HOLLEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 7, 189—191. Compare Abstr., 1900, ii, 275).—When silicon fluoride vapour is passed over heated sodium, reaction takes place according to the equation: $4\text{Na} + \text{SiF}_4 = 4\text{NaF} + \text{Si}$. If excess of silicon fluoride is avoided, there is practically no formation of sodium silicofluoride. When boiled with water and dilute hydrochloric acid, the residue does not, however, consist of pure amorphous silicon, for only about 40 per cent. can be volatilised in a current of chlorine, the remainder consisting principally of silicon dioxide which has been formed in the extraction of the sodium fluoride.

If the crude product is not previously boiled with water, no trace of silicon chloride is formed on heating it in a current of chlorine. This is due to reaction taking place according to the equation: $\text{Si} + 2\text{Cl}_2 + 4\text{NaF} = \text{SiF}_4 + 4\text{NaCl}$.

When sodium is heated in silicon tetrachloride vapour, a violent reaction takes place, but the mass, after extraction with water, also contains about 30 per cent. of silica.

Crystalline silicon is readily obtained according to Kühne's method by covering a mixture of aluminium powder, sulphur, and fine sand in a Hessian crucible with a layer of magnesium powder and igniting by means of a Goldschmidt cartridge. Dilute hydrochloric acid extracts the aluminium sulphide from the residue, and crystalline silicon containing only 3 per cent. of products not volatile in chlorine is obtained. This method is recommended for the preparation of silicon chloride (compare this vol., ii, 331). H. M. D.

Reduction to Carbon of Chemically-combined Carbonic Acid. Electrochemical Changes with Solid Substances. FRITZ HABER and STANISLAW TOLLOZKO (*Zeit. anorg. Chem.*, 1904, 41, 407—441).—Solid sodium hydroxide was fused in an iron dish; it was then cooled, and, as soon as it solidified, was electrolysed by a

current of 0.15 ampere and 11 volts, and finally at 200° with 1 ampere and 5 volts. The yield of sodium was 39 to 46 per cent.

Barium chloride was electrolysed at a temperature 400° below its melting point. When barium carbonate is added to barium chloride, carbon is formed at the cathode in quantitative amount. By aid of sodium, barium carbonate is readily converted into oxide, whilst carbon separates. Barium chloride and barium carbonate were fused together in a nickel crucible, allowed to cool, and then electrolysed at 550–600°, the cathode consisting of iron, platinum, or graphite. Carbon separated in a dendritic form. The *E.M.F.* between 550° and 580° varied from 6 to 10.4 volts, whilst the current strength varied from 22 to 45×10^{-3} amperes. In the experiments with graphite electrodes, the latter were not attacked.

During the electrolysis of barium chloride in a Hempel furnace, carbon was formed at the cathode, owing probably to the action of carbon dioxide and oxygen present in the heating gases on barium chloride, a reaction which proceeds thus: $\text{BaCl}_2 + \text{CO}_2 + \text{O} = \text{BaCO}_3 + \text{Cl}_2 - 11850 \text{ cal.}$ The analogous reaction with calcium chloride, proceeding according to the equation $\text{CaCl}_2 + \text{CO}_2 + \text{O} = \text{CaCO}_3 + \text{Cl}_2 + 1550 \text{ cal.}$, was studied. Chlorine is also produced in an analogous manner by the action of carbon dioxide and oxygen on sodium chloride.

No carbon was obtained when barium chloride was electrolysed in an electric furnace at about 600° in an atmosphere of nitrogen.

For the formation of barium and nickel chlorides as products of the electrolysis of solid barium chloride with nickel anodes, a polarisation of 2.65 volts would be expected according to the equation: $\text{Ba} + \text{NiCl}_2 = \text{BaCl}_2 + \text{Ni} + 122400 \text{ cal.}$ The value 1.9 volts was found corresponding with the free energy of formation of solid barium chloride and nickel from the reaction $2\text{BaCl} + \text{NiCl}_2 = 2\text{BaCl}_2 + \text{Ni}$; the reaction $\text{Ba} + \text{BaCl}_2 = 2\text{BaCl} + 34600 \text{ cal.}$ corresponds with 0.7 volt.

Determinations of the *E.M.F.* of two solid Daniell cells, $\text{PbCl}_2/\text{AgCl}$, agreed with the calculated value 0.519 volt. A. McK.

Action of Bromine on Alkali Hydroxides and the Electrolysis of Alkali Bromides. HORST KRETZSCHMAR (*Zeit. Elektrochem.*, 1904, 10, 789–817).—The first product of the action of bromine on an alkali hydroxide is always a hypobromite, the reactions being $\text{Br}_2 + \text{OH}' \rightleftharpoons \text{HBrO} + \text{Br}'$ and $\text{HBrO} + \text{OH}' \rightleftharpoons \text{BrO}' + \text{H}_2\text{O}$. Solutions of alkali hypobromites are always hydrolysed to a considerable extent, and therefore contain free alkali, hypobromous acid, and bromine, unless there is a very large excess of alkali. Hypobromites are oxidised by free hypobromous acid to bromates, thus: $2\text{HBrO} + \text{MBrO} = \text{MBrO}_3 + 2\text{HBr}$. This reaction differs from the analogous reaction with hypochlorite in having a velocity constant about 100 times greater, and in the fact that it takes place in slightly alkaline solutions (owing to the hydrolysis of the hypobromites). Hypobromites and hypochlorites are nearly equally stable in solutions which contain more than 0.1 gram-molecule of alkali hydroxide per litre.

When a neutral solution of an alkali bromide is electrolysed, bromine is first formed at the anode; this bromine combines with the free

alkali formed at the cathode, giving hypobromite, the concentration of which increases at first, but soon reaches a constant value owing to the hypobromite being converted into bromate as fast as it is formed. When the stationary condition is attained, about 9 per cent. of the current is used in evolving oxygen at a smooth platinum anode, but only about 1 per cent. at a platinised anode. The yield of bromate in the latter case is practically theoretical. The limiting concentration of hypobromite increases with increasing concentration of bromide, higher current density, and lower temperature.

In alkaline solutions, the phenomena are similar, but more oxygen is evolved.

In neutral or slightly alkaline solutions, the formation of bromate is regarded as being practically entirely a secondary reaction due to the oxidation of hypobromite by hypobromous acid, the evolution of oxygen being due to the discharge of hydroxyl ions. The concentration of the hydroxyl ions at the anode is determined by the equilibrium with bromine given at the beginning of the abstract. In presence of excess of alkali, the formation of bromate is mainly due to a primary oxidation of hypobromite by anodic oxygen, $\text{NaOBr} + 2\text{O} = \text{NaBrO}_3$. That this reaction really occurs was proved by the electrolysis of a solution of hypobromous acid; the two possible reactions at the anode are: $\text{BrO}' + 4\text{OH}' + 4F = \text{BrO}_3' + 2\text{H}_2\text{O}$ and $6\text{BrO}' + 3\text{H}_2\text{O} + 6F = 6\text{H}' + 2\text{BrO}_3' + 4\text{Br}' + 3\text{O}$. The second involves the formation of bromide at the anode; the experiments showed that none was produced, hence the direct formation of bromate at the anode takes place in accordance with the first equation, whereas the second represents the nature of the change in the case of chlorate (Abstr., 1902, ii, 642). T. E.

Electrolysis of Alkali Chlorides in presence of Fluorine Compounds. FRITZ FOERSTER and ERICH MÜLLER (*Zeit. Elektrochem.*, 1904, 10, 781—783).—With reference to a process recently patented for the production of chlorates by the electrolysis of a solution of an alkali chloride to which hydrofluoric acid has been added, it is shown that the fluorine has no specific action, the results being merely those obtained by electrolysing a solution made slightly acid by any other means. T. E.

Preparation of Pure Sodium Hydroxide for Laboratory Purposes. FRIEDRICH W. KÜSTER (*Zeit. anorg. Chem.*, 1904, 41, 474—476).—A large, flat-bottomed glass dish of about 50 cm. diameter is filled several centimetres deep with water. In the centre of this is placed a dish made of platinum, silver, or nickel, and capable of containing 500—1000 c.c., and above this, supported by a tripod, a funnel of nickel gauze in which lumps of clean sodium are placed. The funnel and the empty dish are covered with a bell jar (the diameter of which is smaller than that of the flat-bottomed vessel containing the water), which is supported on pieces of glass rod. The sodium is quickly acted on by the water vapour, the hydrogen formed escaping under the bell jar, and the sodium hydroxide formed gradually dropping into the dish under the nickel gauze. A. McK.

Action of Heat on Alkali Phosphates. A. BOIDIN (*Chem. Centr.*, 1904, ii, 1192; from *Bull. Assoc. Chim. Sucr. Dist.*, 22, 112—116).—Disodium hydrogen phosphate, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, is readily decomposed, and the dialkali phosphates behave at high temperatures as if they were dissociated into monoalkali phosphates and alkali hydroxides. Disodium phosphate is basic towards litmus, but if uric acid, which is almost neutral to litmus, is added, the solution becomes acid owing to the formation of monosodium phosphate; the phosphate is also decomposed by carbon dioxide. The alkalinity of a solution of disodium phosphate appears to be dependent on the temperature; with phenolphthalein, it gives a rose coloration, which becomes purple if the solution is warmed, but on cooling it regains the original tint. The results of experiments on the titration of decinormal solutions of disodium phosphate with acid, using phenolphthalein as indicator, showed that as the temperature of the solution is raised, the quantity of acid required for neutralisation increases. The decomposition of the phosphate is complete at 135° , since the rotatory power of dextrose is decreased by a dilute solution at this temperature by the same amount as by sodium hydroxide solution, although in both cases the reducing power is not affected; lævulose is formed on fermentation and one-fifth of the dextrose is not attacked. The alkalinity of disodium hydrogen phosphate is less at 100° , and its effect on the rotatory power of dextrose is also less; like the corresponding potassium salt, however, it is strongly alkaline at this temperature.

E. W. W.

Colloidal Silver Salts. CARL PAAL and FRANZ VOSS (*Ber.*, 1904, 37, 3862—3881. Compare *Abstr.*, 1902, i, 653, ii, 500; this vol., ii, 180).—Colloidal silver salts may be prepared by the method previously described, using alkali protalbates or lysalbates. The latter may be advantageously prepared with a somewhat higher proportion of alkali by the prolonged action of alkali hydroxide on egg-albumin, the excess of hydroxide being removed by dialysis.

Colloidal silver carbonate, prepared by dissolving silver lysalbate or protalbate in sodium carbonate and dialysing, forms a white, opalescent solution, and on evaporation yields the hydrosol in glistening scales, slightly dark in colour owing to the formation of some silver hydrosol, and dissolving readily in water. The dry product may contain as much as 48 per cent. of silver carbonate. Sodium chloride does not precipitate the silver, but forms colloidal silver chloride on heating.

Colloidal silver phosphate, prepared in similar manner, forms a yellow, milky solution and yields the solid hydrosol in yellow, transparent scales on evaporation.

Colloidal silver sulphide may be prepared by dissolving silver protalbate or lysalbate in ammonium sulphide, and may be concentrated by precipitation with hydrochloric acid. The solid hydrosol forms black granules containing as much as 74.6 per cent. of silver sulphide insoluble in water, but dissolving readily in dilute alkali hydroxides or carbonates. The solution is black, appearing dark brown in thin layers (compare Winssinger, *Abstr.*, 1888, 911).

The colloidal silver haloids are best prepared by the addition of

sodium haloid to colloidal silver hydroxide obtained from silver lysalbate. The solutions are opalescent, and yield slightly coloured solid hydrosols containing as much as 90 per cent. of silver haloid, and dissolving readily in cold water. Nitric acid forms a precipitate, which is redissolved by sodium carbonate. Ammonia, potassium cyanide, or sodium thiosulphate destroys the opalescence, forming true solutions (compare Lottermoser, this vol., ii, 31; and Lobry de Bruyn, *Abstr.*, 1900, ii, 136). C. H. D.

So-called Magnesium Peroxide. OTTO RUFF and EMIL GEISEL (*Ber.*, 1904, 37, 3683—3688. Compare D.R.-P. 107246).—Attempts have been made to prepare pure magnesium peroxide by the addition of pure sodium hydroxide to magnesium sulphate solution in the presence of hydrogen peroxide. Even when a large excess of the latter is used, the precipitate in the moist state has the ratio $\text{MgO} : \text{O} = 1 : 0.67$. Drying the precipitate reduces the proportion of peroxidic oxygen, and a product is obtained which has the composition $\text{MgO}, \text{MgO}_2, \text{aq.}$ The dried product readily loses oxygen at 25° or 37° , and at atmospheric pressure, but even after 22 days the ratio $\text{MgO} : \text{O}$ was $1 : 0.39$, and the ratio appears to remain constant at $1 : 0.35$, corresponding roughly with the formula $\text{MgO}_2, 3\text{MgO}, \text{aq.}$

The decomposition is more rapid in the presence of water.

J. J. S.

Phosphorescent Zinc Sulphide. WILLEM P. JORISSEN and WILHELM E. RINGER (*Ber.*, 1904, 37, 3983—3985).—The purer zinc sulphide is, the less tendency to phosphorescence does it show; the presence of traces of other metals increases the tendency to phosphorescence. The results obtained by Grüne (this vol., ii, 732) and by Hofmann and Ducca (this vol., ii, 690) are analogous to those obtained with the sulphides of the metals of the alkaline earths. A. McK.

Complex Zinc Salts. F. KUNSCHERT (*Zeit. anorg. Chem.*, 1904, 41, 337—358).—The condition of zinc and of copper in solutions of complex salts of those metals was investigated by Bodländer and Eberlein's method (this vol., ii, 401). For the electrometric investigation of the formulæ of the various complex salts, the electrode used was not made of the metal present in the complex ion but of some other metal not attacked during the experiments. Solutions of zinc in ammonium oxalate, potassium oxalate, sodium hydroxide, and potassium cyanide respectively were examined.

Concentrated solutions of ammonium and potassium oxalates contain the complex ion $\text{Zn}(\text{C}_2\text{O}_4)_3$; more dilute solutions contain the ion $\text{Zn}(\text{C}_2\text{O}_4)_2$. For the separation of zinc from solutions of oxalates, an *E.M.F.* is required corresponding with the formula $E = 1.006 - 0.029 \log D / (\text{C}_2\text{O}_4)^3$, where D is the concentration of the zinc salt and (C_2O_4) that of the simple oxalate ions in solution.

The stability constants of the complex $\text{Zn}(\text{C}_2\text{O}_4)_3$ ions is 1.4×10^8 , and their free energy of formation from the single ions is 10900 cal. The solubility of zinc oxalate in water is 7×10^{-5} .

In alkaline solutions, zinc is present chiefly in the form of the

ions ZnO_2'' , which are partially hydrolysed into the ions HZnO_2' and OH' .

The tension of zinc towards an alkali zincate solution is expressed by $E = 1.130 - 0.029 \log D / (\text{OH})^4$ relatively to the normal hydrogen electrode, where D represents the concentration of the zincate and (OH) that of hydroxyl ions in gram-mols. per litre.

The stability constant of the complex HZnO_2 is 2.5×10^{12} , and its free energy of formation from the single ions at 18° is 16,520 cal.

In cyanide solutions, the ions are $\text{Zn}(\text{CN})_4$ and $\text{Zn}(\text{CN})_3$.

The tension of zinc towards potassium cyanide solutions is expressed by $E = 1.287 - 0.029 \log D / (\text{CN})^3$, where D represents the concentration of the dissolved zinc double salt and (CN) that of the cyanogen ions in gram-mols. per litre.

The stability constant of the complex $\text{Zn}(\text{CN})_3$ is 3.3×10^{17} , and its free energy of formation from the single ions at 18° is 23,300 cal.

A. McK.

Constitution of Lead-Tin Alloys. OTTO SACKUR (*Chem. Centr.*, 1904, ii, 1022; from *Arb. Kais. Ges.-A.*, 22, 187—204).—The hypothesis that alloys of lead and tin consist of solid solutions which are not mutually soluble in all proportions is supported by the results obtained by determining the state of equilibrium when lead and tin are precipitated from solutions of their salts by means of their alloys. It has been found that lead in alloys containing more than 10 per cent. has the same solution tension as the pure metal, but when the quantity of lead is decreased the solution tension also falls. The solution tension of tin in alloys in which more than 3 per cent. is present is identical with that of the pure metal. The solubility of tin in solid lead is, therefore, less than that of lead in solid tin. The solid alloys probably consist of mixtures of saturated and unsaturated solid solutions of variable composition.

E. W. W.

Solutions of Copper in Potassium Cyanide. F. KUNSCHERT (*Zeit. anorg. Chem.*, 1904, 41, 359—376. Compare preceding page).—Solutions of copper in potassium cyanide contain the ions $\text{Cu}(\text{CN})_4'''$, and to a less extent the ions $\text{Cu}(\text{CN})_3''$.

The tension of copper towards potassium cyanide solution is expressed by $E = 1.130 - 0.0575 \log D / (\text{CN})^4$.

The stability constant of the copper cyanogen ion is 2×10^{27} , and its free energy of formation from the single ions is 36,300 cal., both those values being greater than those found for zinc.

A. McK.

Electrolysis of Solutions of Copper Sulphate. FRITZ FOERSTER and GIULO COFFETTI (*Zeit. Elektrochem.*, 1904, 10, 736—741).—Bose (*Abstr.*, 1899, ii, 349) observed two cathodic decomposition points in solutions of cupric salts. The authors describe some experiments which show that at cathode potentials below the upper point cuprous oxide is deposited from neutral solutions of copper sulphate and cuprous sulphate is formed in acid solutions. The phenomena are best observed in hot solutions, because the concentration of the cuprous ions in equilibrium with cupric ions is greater at higher temperatures.

The observations are best explained by assuming that the reaction $\text{Cu}'' - F = \text{Cu}'$ takes place at the cathode so long as the solution in contact with it contains less than the quantity of cuprous ions corresponding with the equilibrium $2\text{Cu}' \rightleftharpoons \text{Cu} + \text{Cu}''$. Cuprous ions are constantly removed from the neutral solutions by hydrolysis (owing to which cuprous oxide is precipitated), and from acid solutions by oxidation by atmospheric oxygen. At a copper anode, similarly, the copper dissolves in the cuprous condition until equilibrium is attained, and since the layer of solution in contact with the anode always contains more cupric sulphate than the body of the solution, a greater number of cuprous ions will be formed there than can exist in the more dilute mass of the liquid, and therefore as the concentrated solution diffuses away from the anode copper must be deposited. This explains the fact that the loss of weight of the anode is greater than the gain of weight of the cathode, and also the presence of copper dust in the anode slime. T. E.

Reactions of Salts in Solutions other than Aqueous. ALEXANDER NAUMANN [with ERICH ALEXANDER] (*Ber.*, 1904, 37, 3600—3605).—The solubility of a large number of inorganic salts in ethyl acetate was examined qualitatively.

A saturated solution of mercuric chloride in ethyl acetate at 18° contains 1 gram of mercuric chloride to 3.5 grams of ethyl acetate; the action on it of stannous chloride, hydrogen sulphide, ammonia gas, and cadmium iodide was studied.

A saturated solution of cupric chloride in ethyl acetate at 18° contains 1 gram of cupric chloride to 249 grams of ethyl acetate. Its behaviour with ammonia, hydrogen sulphide, hydrogen chloride, stannous chloride, and cadmium iodide was studied. A. McK.

Stability and Solubility Relations of the Hydrates of Ceric Sulphate. IVAN KOPPEL (*Zeit. anorg. Chem.*, 1904, 41, 377—406).—From determinations of the solubility of the hydrates $\text{Ce}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$, $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, and $\text{Ce}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$, Muthmann and Rölzig found (*Abstr.*, 1898, ii, 376) that the dodecahydrate is stable between 0° and 27.5°, the octahydrate between 27.5° and 72°, and the pentahydrate between 72° and 100°; further, the solubility curves of the dodeca- and the octa-hydrates are concave towards the temperature axis, and the solubility of the octa- and penta-hydrates within ranges of temperature at which they are labile is smaller than that of the hydrates stable within the same ranges of temperature. The results of Muthmann and Rölzig are, according to the author, incorrect.

The hydrate $\text{Ce}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$, obtained by the slow evaporation of a concentrated solution of ceric sulphate over sulphuric acid at 0°, crystallises in tiny needles. The hydrate $\text{Ce}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, prepared by evaporation of a solution of ceric sulphate at 40—45°, separates in hexagonal prisms. The hydrate $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ is best prepared by warming at 45—50° a solution of the anhydride of ceric sulphate which has previously been saturated at 0°. The existence of the hydrate $\text{Ce}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ is doubtful. The hydrate $\text{Ce}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ is best prepared by heating at 70—100° a solution of ceric sulphate

which has previously been saturated at a low temperature; it forms monoclinic prisms. The hydrate $\text{Ce}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ is conveniently prepared by agitating the enneahydrate with a little water at 70° for about 48 hours, and then drying the mass at the same temperature.

The solubility in water at various temperatures of the various hydrates enumerated was determined. The results, which are depicted by curves, also indicate the stability relations of the hydrates.

A. McK.

The Atomic Weight of Aluminium. ÉMILE KOHN-ABREEST (*Compt. rend.*, 1904, 139, 669—671).—The method previously employed (compare this vol., ii, 261) for the estimation of aluminium in aluminium powder, namely, weighing as water the hydrogen evolved by the action of dilute hydrochloric acid on a known weight of the powder, can conversely be used to determine the atomic weight of aluminium if pure aluminium or aluminium containing a known quantity of impurities is used; for this purpose, a specimen of aluminium containing 98.68 per cent. of the metal was dissolved in dilute hydrochloric acid (1:10), the hydrogen evolved was dried and passed over heated copper oxide, and the water collected and weighed in tubes filled with glass beads moistened with sulphuric acid. The atomic weight of aluminium as determined by this method (seven experiments) is 27.05 ($\text{H}=1$, $\text{O}=15.88$); and the value obtained by weighing the alumina formed from a known weight of aluminium is 27.09.

M. A. W.

Structure of Alloys. Part I. Aluminium Alloys. WILLIAM CAMPBELL (*J. Amer. Chem. Soc.*, 1904, 26, 1290—1306).—A study of the alloys of aluminium with copper has led to the following conclusions. The series of alloys containing between 0 and 54 per cent. of copper has a eutectic point when about 32 per cent. of copper is present. In alloys containing 32—54 per cent. of copper, crystals of the compound Al_2Cu occur in the eutectic mass. As the proportion of copper increases beyond 54 per cent., the mass of the compound Al_2Cu gradually decreases, whilst a new constituent simultaneously increases until 78 per cent. of copper is present. It is uncertain whether this new constituent is AlCu , Al_2Cu_3 , or AlCu_2 . Alloys containing 83—90 per cent. of copper form solid solutions which at a lower temperature undergo a change, the nature of which depends on whether the alloy contains more or less than 87 per cent. of copper, this being the eutectoid point. Alloys containing between 92 and 100 per cent. of copper form solid solutions, isomorphous with copper, and undergo no rearrangement in the solid state.

The paper is illustrated with microphotographs.

E. G.

Electrolytic Iron. A. SKRABAL (*Zeit. Elektrochem.*, 1904, 10, 749—752).—Electrolytic iron of type A is white, compact, and extremely hard; it is obtained by electrolysis of a ferrous salt with an iron anode and a small current density. Type B is greyer in colour, less compact, and softer than type A; it is obtained by using a platinum anode, a large current density, and a solution of some

complex ferrous salt. Between these two extremes there is a series of intermediate qualities of iron obtained by combinations of the conditions mentioned. Iron of type *A* (obtained by electrolysing a solution of very pure ferrous ammonium sulphate with a platinum cathode, an anode of electrolytic iron, and an *E.M.F.* of about 0.4 volt) is silvery-white and sometimes distinctly crystalline. It dissolves very slowly in warm dilute sulphuric acid and rusts in moist air.

Occasionally specimens are obtained which are hardly attacked by acids or haloids. Type *A* iron is always very hard (it usually scratches glass) and brittle, but it loses these qualities when heated to redness. When the iron is exposed to air, it slowly loses hydrogen, or more rapidly when it is immersed in hot water; this loss of hydrogen does not diminish its hardness and brittleness. The author takes the view that electrolytic iron of type *A* is γ -iron; it is therefore in unstable equilibrium at the ordinary temperature. When heated, it changes into the stable α -iron, which is soft. It cannot be hardened by heating and sudden cooling owing to the high temperature at which γ -iron changes into the β -form in pure iron. The presence of large quantities of hydrogen is attributed to the greater solvent action of γ -iron, which is known to dissolve carbon much more readily than α -iron.

T. E.

The Transformation Temperatures of Steels. GEORGES CHARPY and LOUIS GRENET (*Compt. rend.*, 1904, 139, 567—568).—A comparison of the results obtained by the authors, by Boudouard (compare this vol., ii, 127, 262), and by Belloc in the determination of the transformation temperatures of steels, by the dilatometric, the electric resistance, and the thermoelectric methods respectively, shows that the thermoelectric and dilatometric methods give concordant results in the case of soft steels only, whilst the electric resistance and dilatometric methods give results which agree within the limits of experimental error.

M. A. W.

Cobalt Chloride. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. Roy. Belg.*, 1904, 832).—The solution of cobalt chloride in ethylene glycol exhibits a purplish-violet colour, but when exposed to sunlight for several weeks the solution develops a bluish-violet colour, although only the dihydrated salt can be isolated from it. This appears to support the view that hydrated cobalt salts may exist in several allotropic forms.

T. A. H.

Synthesis of Sulphates by Spring's Process. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. Roy. Belg.*, 1904, 833. Compare this vol., ii, 472).—Nickel and cobalt oxides were separately crushed in contact with sodium hydrogen sulphate in porcelain mortars. In each case, the corresponding sulphate was formed. Similarly, the hydrated uranium oxide, $\text{UO}_3 \cdot \text{H}_2\text{O}$, gave rise to the sulphate, $(\text{UO}_2)\text{SO}_4 \cdot 3\text{H}_2\text{O}$,

when crushed with either sodium or potassium hydrogen sulphate.

T. A. H.

Atomic Weight of Tungsten. EDGAR F. SMITH and FRANZ F. EXNER (*J. Amer. Chem. Soc.*, 1904, 26, 1082—1086).—The atomic weight of tungsten has been determined in the following manner. A weighed quantity of pure tungsten hexachloride was placed in a crucible and treated with distilled water. At a temperature of 60°, the decomposition proceeded quietly with formation of the hydrated oxide. When the mass was dry, a few drops of strong nitric acid were added and afterwards removed by evaporation. The residue was ignited for half an hour at a dull red heat and allowed to cool in the desiccator. Seven series of experiments (including 27 determinations) were made, a different sample of the hexachloride being used in each. Other experiments (23 in number) were carried out in which pure tungsten, obtained by reducing the trioxide in an atmosphere of hydrogen, was reoxidised by ignition in contact with the air, and the resulting trioxide weighed. The results of all these experiments are tabulated. The mean atomic weight of tungsten obtained from the hexachloride experiments was 184.04, whilst that from the oxidation of the metal was 184.065, giving an average value of 184.05 ($O=16$; $Cl=35.45$). E. G.

Structure of Alloys. Part II. Certain Ternary Alloys of Tin and Antimony. WILLIAM CAMPBELL (*J. Amer. Chem. Soc.*, 1904, 26, 1306—1315).—The alloy composed of 25 per cent. of antimony and 75 per cent. of tin, which contains cubes of the compound $SbSn$ distributed throughout its mass, was taken as a basis, and portions of it were alloyed with each of the following metals: lead, cadmium, bismuth, copper, silver, zinc, arsenic, and aluminium. The alloys produced can be divided into three groups according to their structure.

(1) In these alloys, cubes of the compound $SbSn$ are imbedded in a ground mass of tin dendrites, surrounded by the eutectic alloy of tin and the third metal. This structure occurs with lead and bismuth.

(2) Cubes of the compound $SbSn$ and crystals of a compound of tin and the third metal are formed in the eutectic alloy of the latter compound with the third metal. This structure is produced with copper and silver. When arsenic is the third metal, the ground mass is a solid solution of tin.

(3) A compound of antimony and the third metal is formed. In the case of aluminium, the ground mass consists of crystals of the eutectic alloy of this metal with tin. In the case of zinc, and probably also of cadmium, the ground mass consists of crystals of the compound $SbSn$ and a solid solution rich in tin.

The paper is illustrated with microphotographs.

E. G.

Stannic Compounds. ITALO BELLUCCI and N. PARRAVANO (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 307—314).—The apparently perfect analogy indicated by the formulæ of chlorostannic and chloroplatinic acids, which both crystallise with six molecules of water, is borne out by the chemical behaviour of the acids and of their salts, the stannic derivatives being, however, far less stable than the platinum ones.

Thus when the former is heated in a vacuum at 100° in presence

of potassium hydroxide, it loses one molecule of hydrogen chloride, forming the bibasic pentachloroplatinic acid, whilst chlorostannic acid in a vacuum in presence of potassium hydroxide decomposes at the ordinary temperature, yielding stannic chloride; the latter change also proceeds slowly in the air.

Chlorostannic acid cannot be titrated, because, as is shown by conductivity measurements of its solutions to which increasing proportions of sodium hydroxide are added, it undergoes hydrolytic decomposition in solution. Chloroplatinic acid, on the other hand, is a strong bibasic acid. Potassium stannichloride is also instantaneously hydrolysed in dilute solutions, whilst the platinichloride withstands long boiling in aqueous solution without change.

T. H. P.

Constitution of the Stannates. ITALO BELLUCCI and N. PARRAVANO (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 324—331. Compare preceding abstract).—On heating crystallised sodium stannate, $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$, it loses its $3\text{H}_2\text{O}$, giving the anhydrous stannate, which does not dissolve unchanged in water and does not tend to take up water so as to form the original salt.

Contrary to the statements of various authors, crystallised potassium stannate (with $3\text{H}_2\text{O}$) cannot be completely dehydrated by heating, as it begins to decompose, forming potassium hydroxide and stannic acid, as soon as any water is evolved. The heating observed when the ignited salt is treated with water is due solely to the action of the latter on the potassium hydroxide.

These facts indicate that the three molecules of water associated with the molecule of an alkali stannate are not merely water of crystallisation, but are more intimately connected with the salt. The latter has probably a structure similar to that of the hexahydroxyplatينات, namely, $\text{X}_2\text{Sn}(\text{OH})_6$.

Hexahydroxyplatinic acid, $\text{H}_2\text{Pt}(\text{OH})_6$, is a stable compound and is reduced to platinic hydroxide only by heating for some time at 100° , whilst the corresponding hexahydroxystannic acid is very unstable and is converted into stannic hydroxide on exposure to the air.

That the stannates are really derivatives of hexahydroxystannic acid is confirmed by the fact that the insoluble compounds formed from them by double decomposition have the formula $\text{X}''\text{Sn}(\text{OH})_6$.

T. H. P.

Preparation of Solid Titanous Chloride. PETER SPENCE & SONS (D.R.-P. 154542. Compare Polidori, *Abstr.*, 1899, ii, 295).—Solid titanous chloride, $\text{TiCl}_3 \cdot 6\text{H}_2\text{O}$, is most readily prepared by electrolysing a 25 per cent. solution of titanous chloride, employing a potential difference of 3—4 volts and a current density of 2 amperes per sq. dm., and evaporating under reduced pressure until the solution has a sp. gr. 1.5 at $60\text{--}70^\circ$, when crystals of titanous chloride separate on cooling, and a further quantity is obtained on concentrating the mother liquor.

C. H. D.

Extraction of Vanadium from Natural Lead Vanadate, and Preparation of some of its Alloys. H. HERRENSCHMIDT (*Compt. rend.*, 1904, 139, 635—637).—The slag obtained on fusing lead

vanadate from the Santa Marta mines, Spain, with sodium carbonate and carbon contains all the vanadium in the form of sodium vanadate mixed with sodium aluminate and silicate and iron oxide. It is separated as vanadic acid by oxidation in the fused state with atmospheric oxygen and subsequent extraction with boiling water and treatment with sulphuric acid.

Ferrovanadium, containing 83 per cent. of vanadium, is made by igniting in the electric furnace the precipitate obtained by mixing sodium vanadate, iron sulphate, and sodium carbonate in the requisite proportions.

Nickelvanadium containing 25 per cent. of vanadium is obtained by reducing a mixture of vanadic acid and nickel oxide. M. A. W.

Metallic Acids. ROY D. HALL (*J. Amer. Chem. Soc.*, 1904, 26, 1235—1250).—The oxides of columbium and tantalum employed in this investigation were obtained from columbite. A specimen of this mineral from Haddam, Conn., had a sp. gr. 5.75 at 4° and, on analysis, gave the following results:

| | Ta ₂ O ₅ , Cb ₂ O ₅ . | WO ₃ , SnO ₂ . | Fe ₂ O ₃ . | U ₃ O ₈ . | MnO. |
|-----|---|--------------------------------------|----------------------------------|---------------------------------|------|
| I. | 79.75 | 0.32 | 15.11 | 0.23 | 6.69 |
| II. | 79.49 | 0.32 | 15.09 | 0.24 | 5.83 |

The mineral was decomposed by means of strong sulphuric acid. On extracting with boiling water, the oxides of columbium and tantalum were left as a residue together with the oxides of silicon, titanium, tungsten, and tin. This residue was left for several days in contact with a solution of yellow ammonium sulphide. The remaining oxides were dissolved in hydrofluoric acid, and the tantalum and silicon were separated as the double potassium fluorides, the columbium being obtained in the later fractions as the double potassium fluoride and oxyfluoride. It was found that the treatment with ammonium sulphide did not remove the whole of the tin and tungsten. The oxides of columbium and tantalum, prepared from the double fluorides, were therefore fused with sodium carbonate and sulphur. On extracting with water, the columbium oxide remained in the form of an insoluble sodium hydrogen salt. By fusing this compound with potassium hydrogen sulphate and washing the product with boiling water, the columbium oxide was obtained free from tin and tungsten. The oxide was converted into potassium columbium oxyfluoride, which was purified from tantalum by heating it at 150—175° and afterwards dissolving it in water. By repeating this operation, the whole of the tantalum was separated as an insoluble residue. The potassium columbium oxyfluoride thus obtained was found to contain titanium. Smith has shown (*Abstr.*, 1898, ii, 571) that sulphur monochloride dissolves the oxides of columbium, tantalum, and titanium forming crystalline compounds in the case of the first two metals and a liquid with the titanium. A study was made of these reactions with the hope of devising a satisfactory method for removing traces of titanium from columbium. It was found, however, that the titanium could not be separated completely in this way. Columbium oxide free from titanium was obtained eventually by repeated precipitation of a

solution of the oxyfluoride with ammonium hydroxide, the titanium remaining in solution.

When titanium oxide is heated with sulphur monochloride at 200° for several hours in a sealed tube and the product is distilled, the titanium is volatilised, probably as the tetrachloride, and passes over with the sulphur monochloride. Oxide of columbium, under similar conditions, dissolves in the sulphur monochloride and, on cooling, the pentachloride separates in transparent, yellow prisms. On heating the product, the sulphur monochloride passes over first, and the columbium pentachloride distils at $220\text{--}235^{\circ}$. The chloride prepared in this way contains traces of sulphur monochloride, but can be purified by distillation in a current of chlorine. Tantalum pentachloride, prepared in a similar manner, forms nearly white crystals which melt to a pale yellow liquid.

The oxides of titanium, aluminium, and iron are readily converted into volatile chlorides when heated with sulphur monochloride, whilst the oxides of tungsten, vanadium, and molybdenum yield volatile oxychlorides. Oxides of zirconium and tin are changed to volatile chlorides, but require to be heated for a considerable time at a high temperature. Oxides of boron and silicon are not affected, but chromic oxide is slowly converted into the violet chloride.

The use of sulphur monochloride affords a convenient method for preparing the anhydrous chlorides of many elements, and also provides a means of separating those elements which form volatile chlorides from those forming non-volatile chlorides. Sulphur monochloride is also useful for effecting the decomposition of some of the most refractory minerals.

In the course of this investigation, the double potassium fluorides of titanium, zirconium, columbium, and tantalum were submitted to a series of comparative qualitative tests with various reagents, and the results are tabulated.

E. G.

Removal of Oxygen by Platinum. EUGEN GOLDSTEIN (*Ber.*, 1904, 37, 4147—4148).—The power of platinum to absorb oxygen can be excellently demonstrated by melting a platinum wire, about 4 mm. thick, into a Geissler tube so as to project about 1 cm. Then on filling the tube with oxygen, and sparking, the platinum becomes white hot, and in about 2 minutes the oxygen is completely absorbed. E. F. A.

Mineralogical Chemistry.

Bournonite from Sardinia. DOMENICO LOVISATO (*Zeit. Kryst. Min.*, 1904, 40, 97; from *Rend. Accad. Lincei*, [v], 11, ii, 357—361).—A massive mineral, occurring with galena at the Argentiera della Nurra mine at Portotorres, is shown by the following analysis, by C. Rimatori, to be bournonite, and not tetrahedrite as formerly supposed:

| S. | Sb. | As. | Pb. | Cu. | Fe. | Mn. | CaO, MgO. | Total. |
|-------|-------|-------|-------|-------|------|------|-----------|--------|
| 19.14 | 20.70 | trace | 40.73 | 12.22 | 4.59 | 1.35 | traces | 98.73. |

L. J. S.

[Augite] from Canale Monterano, Province Rome. FERRUCCIO ZAMBONINI (*Zeit. Kryst. Min.*, 1904, 40, 49—68).—A crystallographic description is given of various minerals (magnetite, melanite, yellow garnet, olivine, idocrase, biotite, various green pyroxenes, black augite, and sanidine) from the weathered tuffs of Canale Monterano near Bracciano. The black augite gave the following results on analysis :

| SiO ₂ . | TiO ₂ . | Al ₂ O ₃ . | Fe ₂ O ₃ . | FeO. | MnO. | CaO. | MgO. | Na ₂ O. | H ₂ O. | Total. |
|--------------------|--------------------|----------------------------------|----------------------------------|------|-------|-------|-------|--------------------|-------------------|---------|
| 50.88 | 1.02 | 5.36 | 1.21 | 4.67 | trace | 22.96 | 13.78 | 0.50 | 0.34 | 100.72. |

L. J. S.

Physiological Chemistry.

Differences in Electrical Potential in Developing Eggs. IDA H. HYDE (*Amer. J. Physiol.*, 1904, 12, 241—275).—The experiments were made on the eggs of the turtle and of *Fundulus*, and were carried out in relation to the work of others on the influence of electrolytes and ions on development. A difference of electrical potential occurs, which increases as development progresses, between the animal and vegetative poles of the eggs. The *E.M.F.* so generated undergo periodic variations during the phases of segmentation, and are doubtless related to the unstable equilibrium of chromatin and other substances. The alterations and interactions of ions and their associated energies are accompaniments of the physical and chemical changes in the egg, and give expression to their tension action in the form of astral and spindle radiations. W. D. H.

Alkalinity of Blood. OTTO FOLIN (*Zeit. physiol. Chem.*, 1904, 43, 18—20).—The principle and results of the method adopted by Salkowski, and later by Salaskin, for estimating the alkalinity of the blood are disputed. W. D. H.

Blood Proteids. GUSTAV VON BERGMANN and LEO LANGSTEIN (*Beitr. chem. Physiol. Path.*, 1904, 6, 27—39).—In dogs killed in active digestion, the blood contains a variable percentage of nitrogen after the separation of the coagulable proteids by boiling, acidifying, and filtering. What this residual nitrogen is contained in is discussed. The statement is made that albumoses are contained in normal blood during digestion in small but appreciable and physiologically important quantities. W. D. H.

Action of Naphthalene- β -sulphonic Chloride on the Blood. GUSTAV VON BERGMANN (*Beitr. chem. Physiol. Path.*, 1904, 6, 40—43).—The possibility that some of the residual nitrogen of the blood (see preceding abstract) may be contained in amino-acids and polypeptides, which recent research has shown are of importance in the synthesis of the body proteids, led to an attempt to separate these substances by the

use of naphthalene- β -sulphonic chloride. A compound was obtained which, on analysis, gives numbers which will not fit in with any known substance. The work is to be continued. W. D. H.

Diastrases and Anti-diastrases in Blood Serum. M. ASCOLI and A. BONFANTI (*Zeit. physiol. Chem.*, 1904, 43, 156—164).—By immunising rabbits with pancreatin, an anti-substance against pancreatic diastase is obtained in the serum. The formation of the anti-diastrase is, however, variable. By prolonged immunisation, the anti-diastrase disappears. It exhibits a variable inhibitory action on the blood diastrases of other species of animals, but not on that of the rabbit. In some of the rabbits so treated, the amylolytic action of the fresh blood-serum is lessened, but the diminution does not correspond with the amount of anti-amylase formed. W. D. H.

Oxygen Exchange of the Pancreas. JOSEPH BARCROFT and ERNEST H. STARLING (*J. Physiol.*, 1904, 31, 491—496).—Pancreatic secretion is accompanied by an increased oxygen absorption from the blood by the pancreas. This is shown by examining the blood by the air-pump or by the ferricyanide method. This increased oxidation takes place irrespective of increased flow of blood through the organ. The normal oxidation of the pancreas is much greater than that of the body generally, and about the same as that of the submaxillary gland. W. D. H.

Alcohol as a Food. W. H. GODDARD (*Lancet*, 1904, ii, 1132—1136).—From experiments on dogs, the conclusion is drawn that with moderate doses 95 per cent. of the alcohol given is made use of in the formation of simpler products and the simultaneous liberation of energy, that is, it plays the part of a food. But with increasing doses this number is reduced; in such circumstances, there is a partial failure of the animal body to utilise the amount administered, so that in the final experiments, when the drug was given in excess, nearly 50 per cent. of it was excreted unchanged. W. D. H.

Phosphorus Metabolism. LUDWIG F. MEYER (*Zeit. physiol. Chem.*, 1904, 43, 1—10).—Experiments on dogs show that on a diet poor in phosphorus (powdered meat and white of egg) the proteid requirements of the organism are as completely met as in cases where phosphorised material is abundantly given. Proteid is put on even in cases where the phosphorus balance is negative. Any definite relationship between the excretion of nitrogen and phosphorus is absent. An increase of phosphorus (as phosphates) in the food leads to a retention of phosphorus in the body. W. D. H.

Feeding Experiments on Dogs without a Pancreas. GUSTAV EMBDEN and H. SALOMON (*Beitr. chem. Physiol. Path.*, 1904, 6, 63—67. Compare Abstr., 1902, ii, 677).—Alanine, as previously shown, given to dogs without a pancreas increases the output of sugar. The same is true for lactic acid, glycine, and asparagine. Urea produces diuresis, but no increase of the sugar excreted. W. D. H.

Auto-digestion of Pepsin. AMEDEO HERLITZKA (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 51—57).—In order to ascertain whether pepsin is a true proteid substance or only closely allied to the latter, the author has subjected a solution of carefully purified pepsin, which showed no biuret reaction, to a temperature of 40° in presence of 0.2 per cent. of hydrochloric acid. After remaining under these conditions for a period of from 11 to 40 hours, the solutions all gave the biuret reaction, so that peptone is formed from pepsin by auto-digestion. By experiments in which the pepsin solution acts on albumin, it is found that the auto-digestion coefficient increases as time goes on.

Hence one part of the pepsin acts on another with a peptonising action just as in a true auto-digestion, and pepsin is hence a true proteid.
T. H. P.

Glycolysis. P. PORTIER (*Ann. Inst. Pasteur*, 1904, 18, 633—643).—In the presence of sufficient antiseptic (1 per cent. sodium fluoride), the expressed juice of various organs produces no glycolysis at 36° during two days' incubation. No glycolysis occurs during 2 to 3 hours' incubation, even if no antiseptic or only chloroform is added. The juice of organs rich in glycogen shows an increase of reducing power, owing to the action of the amylase and maltase of the tissues. Alcohol was never formed in appreciable quantities. The conclusions of Stoklasa and Simacek are disputed.
W. D. H.

Hydrolysis of Fresh and Self-digested Glands. PHOEBUS A. LEVENE (*Amer. J. Physiol.*, 1904, 12, 276—296).—The cleavage products of proteids are different when the hydrolysis is carried out by acid and by autolysis. One explanation of this is found in the recent discoveries of arginase, guanase, and similar enzymes. In the present research, the pancreas, spleen, and liver were employed, both fresh and after autolysis, and the basic constituents examined after treatment with 5 per cent. sulphuric acid. The results with the pancreas are as follows: from the fresh glands, guanine and a smaller amount of adenine were formed; xanthine and hypoxanthine were absent, or nearly so. In the digested gland, the total purine bases were less, little guanine was found, no adenine, but appreciable amounts of xanthine and hypoxanthine. Among the pyrimidine bases, the fresh gland yielded uracil and cytosine, but no thymine; the digested gland yields uracil only. Of the hexon bases, arginine and lysine were obtained from the fresh gland, but not from the digested organ, their place being taken by tetramethylenediamine. Finally, the digested gland yields more ammonia than the fresh gland.

The results with the liver and spleen were very similar, but some differences of detail are noticed.
W. D. H.

Detection of Guanidine amongst the Products of the Autodigestion of the Pancreas. FR. KUTSCHER and J. OTORI (*Zeit. physiol. Chem.*, 1904, 43, 93—108. Compare Abstr., 1903, i, 666).—The paper largely treats of the method for separating some of the various substances (histidine, arginine, guanidine) obtained as a result of pancreatic autodigestion. Considerable im-

portance is attached to the discovery of guanidine among the products, because it is sometimes undoubtedly formed as the result of normal metabolic processes.

W. D. H.

Autolysis of Ox Testis. JUNICHI MOCHIZUKI and Y. KOTAKE (*Zeit. physiol. Chem.*, 1904, 43, 165—169).—Among the autolytic products separated and identified are ammonia, guanine (?), hypoxanthine, xanthine, thymine, lysine, and choline. Whether leucine and tyrosine are also present is to be the subject of further work.

W. D. H.

Formation of Acetone in the Body. GIUSEPPE SATTA (*Beitr. chem. Physiol. Path.*, 1904, 6, 1—26).—In normal circumstances, small quantities of acetone leave the body in the excretions, but β -hydroxybutyric acid is absent. The latter substance is easily burnt in the healthy body, but it is not regarded as the usual source of the acetone. Numerous experiments with different diets on men are given; no regular relationship between ammonia and acetone formation was found. With absence of carbohydrate food, there is an increase in the excretion of ammonia and uric acid. Acetone formation is inhibited by giving the necessary amount of carbohydrates in the diet. In pneumonia, the acetone decreases and the nitrogen excretion increases. Details are also given of the conditions in other pathological cases. The source of acetone substances is discussed at length, and the conclusion reached is that it is not proteid or carbohydrate, but fat.

W. D. H.

Formation of Sugar in Artificial Perfusion of the Glycogen-free Liver. GUSTAV EMBDEN (*Beitr. chem. Physiol. Path.*, 1904, 6, 44—58).—The livers of dogs rendered free from glycogen by the administration of strychnine were perfused with either ox blood or dog's blood. An appreciable increase in the amount of sugar in the blood was noticeable in a few hours. If sugar is added to the blood beforehand, the same increase occurs. After a time, no further increase occurs; but if a fresh lot of blood is then used for perfusing, the same increase is repeated in that. What the substance is which gives rise to sugar is not yet discovered, but the source of the newly-formed sugar is probably both in the blood and the liver.

W. D. H.

The Occurrence of a Volatile, Iodoform-forming Substance during Perfusion of the Liver. MARCO ALMAGIA and GUSTAV EMBDEN (*Beitr. chem. Physiol. Path.*, 1904, 6, 59—62).—The blood used in the experiments described in the preceding abstract yielded on distillation a substance which yielded iodoform with iodine. It is not alcohol or aldehyde, but probably acetone; this, however, was not definitely proved.

W. D. H.

The Nitrogenous Constituents of Flesh. HARRY S. GRINDLEY (*J. Amer. Chem. Soc.*, 1904, 26, 1086—1107).—A considerable portion of raw meat is soluble in cold water; thus 12.14 of the total proteid and 22 per cent. of the total nitrogen are soluble. The nitrogen in

such extracts is about equally divided between proteid and non-proteid substances. The acidity of a solution of flesh increases on the coagulation of its proteids. The proteids of cooked meats are much less soluble in cold water and 10 per cent. solution of sodium chloride. In 0.15 per cent. hydrochloric acid, the solubility in the two cases is about equal; in 0.15 per cent. solution of potassium hydroxide, the cooked proteids are more soluble. Hot water removes from raw meat 0.49 per cent. of proteid, and from boiled meat 6.2 per cent. All these conclusions are founded upon numerous analyses. The nature of the proteid matter in the different extracts has not yet been investigated.

W. D. H.

Serosamucin. GUSTAF VON HOLST (*Zeit. physiol. Chem.*, 1904, 43, 145—155).—*Serosamucin* is the name given to the mucinoid substance which is present in many cases of ascitic fluid. The mucinoid material of synovia may be mixed with nucleo-proteid from the cells, but is a true mucin, having a composition practically identical with that of serosamucin. It is free from phosphorus.

W. D. H.

Osmotic Pressure of Proteids. E. WAYMOUTH REID (*J. Physiol.*, 1904, 31, 438—463).—The osmotic pressure of serum and egg-white per unit concentration of proteid varies in different samples. The same variability is exhibited by solutions of the proteids salted out and dialysed, or crystallised from these fluids. By washing the salted-out or crystallised proteids, solutions of proteids are obtained which give no osmotic pressure. Non-proteid substances in the washings have an osmotic pressure. The presence of osmotic pressure-free proteids in the membrane is necessary to render it impermeable to these substances. Proteid-metabolites produced by bacterial growth will impart osmotic pressure to solutions of proteids previously giving none; this can be again reduced by washing.

W. D. H.

The Physiological Significance of Colloids. RUDOLF HÖBER and DORA GORDON (*Beitr. chem. Physiol. Path.*, 1904, 5, 432—441).—Experiments similar to those described by Freundlich (*Abstr.*, 1903, ii, 533) have been made by adding electrolytes at different rates to such colloidal solutions as egg-albumin or gelatin, and Freundlich's results confirmed. This in conjunction with the Bois-Raymond law of electric excitation of nerves is considered to indicate that the transportation of ions to the excited object (the "plasmahaut") is probably the cause of excitation.

It is shown that the colloid of the "plasmahaut," namely, lecithin, can be narcotised by chloroform, ether, amyl alcohol, &c. Linder and Picton's conclusions (*Trans.*, 1895, 67, 63) as to the mutual retardation of univalent and bivalent cations on the precipitation of arsenious sulphide are confirmed. The anions have no effect; two cations of the same valency have an effect equal to the sum of the two separate ions, but the effect of two cations of different valencies is less than the sum of the effects of the two individual ions.

J. J. S.

Tyrosinase of *Lucilia Cæsar*. C. GESSARD (*Compt. rend.*, 1904, 139, 644—645).—Both tyrosinase and tyrosine can be detected in the larva of *Lucilia Cæsar*, and the larval covering or skin of the nymph, at first white, becomes black owing to the oxidising action of the tyrosinase on the tyrosine; if, however, the white pupæ are kept in a vacuum, the oxydase is inoperative, and no coloration is developed; similar results are obtained with the insects, which are colourless at first and develop a metallic golden-green lustre in the air but remain colourless in a vacuum.

M. A. W.

Heat Contraction in Nerve. T. GREGOR BRODIE and WILLIAM D. HALLIBURTON (*J. Physiol.*, 1904, 31, 473—490).—When a nerve is heated, it shortens very considerably; this is especially the case with frogs' nerves. The same is true for the spinal cord. The shortening as in muscle occurs in a series of steps, and the temperatures at which these successive contractions occur coincide with the coagulation temperatures of the proteids contained in saline extracts of nervous tissues. Special interest attaches to the first step in the contraction; in the frog this occurs at 39—40°; in the mammal, at 47—49°; and in the bird, at 50—53°. A small amount of slow contraction occurs a few degrees below those just mentioned; this corresponds with the stage of opalescence when a proteid solution is gradually heated. The temperatures of the first contraction in nerve or spinal cord correspond closely with those in muscle. They further coincide with those in liver, the method being applicable to tissues like the liver, even although the histological elements have no longitudinal arrangement. The death temperature of muscle is that at which the first proteid coagulates; the same is true for nervous tissues; conduction and electrical response are abolished then. These facts indicate a biological adaptation of the tissue proteids of animals in relation to their normal temperatures, and to the rise of temperature to which they may be safely subjected.

W. D. H.

Decapsulation of the Kidney. ISAAC LEVIN (*Amer. J. Physiol.*, 1904, 12, 304—309).—Removal of the kidney capsule for various kinds of kidney disease is now a frequent surgical proceeding, which is stated to result in benefit. The function of the capsule is unknown. It is suggested that it may be protective against noxious agents, and that the benefit of decapsulation may be counterbalanced by injury due to depriving the kidney of its covering. By the oncometric method, it was found that any stimulus which, like adrenaline, raises the general blood pressure, or like vagus excitation weakens the cardiac force, diminishes the size of the kidney. This effect is greater on a decapsulated kidney than on a normal one, and lasts longer. The capsule acts like an elastic covering, preventing undue filling of the organ with blood. Decapsulation does not apparently injure the renal nerves.

W. D. H.

The Bile of Polar Animals. II. The Bile of the Musk Ox. OLOF HAMMARSTEN (*Zeit. physiol. Chem.*, 1904, 43, 109—126. Compare Abstr., 1903, ii, 86).—The bile of the musk ox contains glyco-

cholic acid, glycocholic acid, and taurocholic acid. The methods of separation and identification of these substances are given in detail.

W. D. H.

The Power of the Liver to Destroy Diphtheria Toxin. T. LAUDER BRUNTON and T. J. BOKENHAM (*J. Pathol. Bacteriol.*, 1904, 10, 50—55).—The liver has the power of diminishing the lethal action of the diphtheria toxin when this is circulated through it, either alone or mixed with blood. In such circumstances, the bile acquires a certain amount of antitoxic power; the juice expressed from the liver has the same power, and the nucleo-proteid separated from the juice has marked antitoxic activity.

W. D. H.

Chemical Theories of Immunity. JULES BORDET (*Ann. Inst. Pasteur*, 1904, 18, 593—632).—A full account of the author's views on the chemical theories of immunity and the properties of *antisensibilisatrices*. The experiments recorded mainly relate to hæmolysis. Ehrlich's view that specific auto-substances are identical with the cellular receptors is disputed.

W. D. H.

A Case of Pentosuria with Excretion of Optically Active Arabinose. RICCARDO LUZZATTO (*Beitr. chem. Physiol. Path.*, 1904, 6, 87—91).—A curious case of *l*-arabinosuria is recorded; this condition, like the more common *r*-arabinosuria, is not a disease, but an anomaly of intermediate metabolism; those who exhibit it enjoy perfect health.

W. D. H.

Action of Adrenaline on the Bladder. T. R. ELLIOTT (*Proc. physiol. Soc.*, 1904, lix; *J. Physiol.*, 31).—The bladder of the cat is fully, and that of the monkey weakly, inhibited by adrenaline; those of the dog, rabbit, and mongoose exhibit no change; that of the ferret is contracted. The response of each bladder to excitation of the hypogastric nerve is identical with that caused by adrenaline. These facts confirm the hypothesis originally put forward by Brodie that adrenaline acts by stimulating sympathetic nerve-endings.

W. D. H.

A Group of Therapeutically Active Acid Amides. G. FUCHS (*Zeit. angew. Chem.*, 17, (xl), 1505—1509).—A discussion, with a review of previous work, on the relative value of the halogen atom, and of the ethyl, hydroxyl, and other groups in various anæsthetics and hypnotics.

Experiments on animals are recorded concerning the sedative action of bromodiethylacetamide (neuronal), bromoethylpropylacetamide, and bromodipropylacetamide. The first named is the most efficacious, and is highly recommended in epilepsy.

W. D. H.

Effect of Intravenous Injections of Sodium Cinnamate. FRANK CHARTERIS and E. PROVAN CATHCART (*J. Pathol. Bacteriol.*, 1904, 10, 56—59).—Sodium cinnamate given intravenously causes a slight permanent increase of mono-nuclear leucocytes. There are no

changes in the marrow, and the slight changes seen in the spleen point to stimulation of that organ. W. D. H.

Action of Pituitary Extracts on the Frog's Circulatory System. PERCY T. HERRING (*J. Physiol.*, 1904, 31, 429—437).—Extracts of the infundibular portion of the pituitary body cause acceleration and augmentation when perfused through the isolated frog-ventricle. Strong extracts cause tonic contraction of the ventricle. If the extract is injected intravenously in a pithed frog, the heart-beat is slowed and diminished. This is abolished by atropine; after atropine, acceleration and augmentation are produced by the injection. This is attributed to the presence in the extract of two substances or groups of substances, one of which stimulates the intrinsic inhibitory nervous mechanism of the heart, the other the intrinsic accelerator mechanism; the action on the former alone is abolished by atropine. The extract also causes vaso-constriction, and as this action is abolished by apocodeine, it is attributed to stimulation of vaso-constrictor nerves. W. D. H.

Antitryptic Action of Serum. E. PROVAN CATHCART (*J. Physiol.*, 1904, 31, 497—506).—The antitryptic action of normal serum is associated with the albumin fraction. Globulins do not possess it, and are, moreover, very slowly attacked by the enzyme. The auto-action is effective with all varieties of proteid. Absolute specificity does not exist, and the existence of partial specificity is questionable. Heating the albumin to 55° for half an hour largely destroys its antitryptic activity, but the antitryptic action of the serum itself is more resistant to heat. Solutions do not deteriorate rapidly, and drying and dialysis have little or no destructive influence.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

The Role of Microbes in Alcoholic Fermentation attributed to Zymase. PIERRE MAZÉ and A. PERRIER (*Ann. Inst. Pasteur*, 1904, 18, 382—384).—Vegetable extracts, fresh or fermented, and fresh animal extracts to which sugar has been added undergo the alcoholic fermentation ; this, however, is not due to a zymase furnished by the cells, as Stoklasa considers, but to various micro-organisms, which, although admittedly present in Stoklasa's experiments, were stated by him to be incapable of producing the fermentation.

W. D. H.

Coagulation of Milk by *Bacillus Coli Communis*. WILLIAM G. SAVAGE (*J. Pathol. Bacteriol.*, 1904, 10, 90—97).—Curdling of milk by this bacillus is due in almost all cases to the formation of acid, presumably lactic acid, by the bacteria. In a few cases of curdling

produced after several days' incubation, the coagulation is ascribed to an enzyme. An enzyme having the power of converting caseinogen into casein can be separated from the bacteria, but in general this plays no part in the initial curdling.

W. D. H.

Origin of Fusel Oil. OSKAR EMMERLING (*Ber.*, 1904, 37, 3535—3538).—Fusel oil is formed from carbohydrates, especially from starch and sucrose, also from pentoses such as arabinose and xylose, and from pentosans, by the action of anaërobic bacteria, which are commonly found on the skins of potatoes. The yield of fusel oil almost disappears if the starch or sucrose is hydrolysed before fermentation. Hydrogen, carbon dioxide, and butyric acid are formed as by-products of the action.

G. Y.

Behaviour of Proteids during Alcoholic Fermentation. LEONID IWANOFF (*Zeit. physiol. Chem.*, 1904, 42, 464—492).—The amount of proteids present in yeast before and after fermentation remains practically the same; it is highly improbable that this is due to a state of equilibrium between proteid synthesis and decomposition. The yeast during fermentation does not synthesise proteids from the non-proteid nitrogenous substances present, although it is able to convert added asparagine into proteids.

When yeast is kept for some time without a nutrient medium, some 40 per cent. of the proteid nitrogen is transformed into non-proteid nitrogen, and on the addition of a glucose nutrient medium some 40—60 per cent. only of the non-proteid is synthesised into proteid nitrogen. It should thus be impossible for the proteid decomposition to be completely obscured by proteid synthesis.

Fermented yeast undergoes proteolysis much less readily than unfermented yeast, and the addition of fermented to unfermented retards its autolysis. This retarding substance is a volatile product of fermentation, its activity is not destroyed by filtration through a Chamberland filter, but is largely interfered with by boiling. The substance is not alcohol, but probably an aldehydic by-product. The addition of monopotassium phosphate not merely entirely negates the retarding influence of this substance, but considerably increases the rate of autolysis.

The decomposition of proteids during fermentation observed by Mitscherlich, Thénard, Pasteur, Liebig, Nageli, Duclaux, Schützenberger, and Detmer was largely due to their not working with sterilised materials, and to the long time allowed for the fermentation to proceed.

J. J. S.

Preparation of Yeast Poor in Glycogen and its Use for the Detection of Sugar in Urine. EDUARD BUCHNER and SIGURD MITSCHERLICH (*Zeit. physiol. Chem.*, 1904, 42, 554—562).—Many "bottom" yeasts contain appreciable amounts of glycogen, and this interferes with many of the reactions in which the yeast is used; for example, a press extract obtained from such a yeast undergoes auto-fermentation with evolution of carbon dioxide without the addition of any sugar.

A yeast practically free from glycogen may be obtained by exposing the pressed and sifted yeast in thin layers for a day at 2°, or for 8 hours at 20° or for 3—4 hours at 45°. The presence of air is not necessary, as the operation may be performed in a vacuum or in an atmosphere of carbon dioxide with similar results. The activity of the yeast is not destroyed by this treatment, but in some cases appears to be strengthened. The extract obtained from such a yeast is of considerable use in detecting and estimating sugar in urine. J. J. S.

Origin of Carbon Dioxide in Seeds during Germination. EDOUARD URBAIN (*Compt. rend.*, 1904, 139, 606—608).—According to Connstein, Hoyer, and Wartenberg (compare Abstr., 1903, i, 218) and to Nicloux (compare this vol., ii, 508, 635), the hydrolysis in a sterile medium of the fats in castor oil seeds is dependent on the presence of carbon dioxide. The author finds that the carbon dioxide does not come from the air, for if the seeds are ground with a 1 per cent. solution of chloral hydrate and sealed in a flask which has been freed from air, 52—61 per cent. of the fats are hydrolysed after four days and the flask contains carbon dioxide. Comparative experiments on the hydrolysis of castor oil by the action of cytoplasm only, or of cytoplasm and aleurone in a sterile medium deprived of air, show that the origin of the carbon dioxide is due to the hydrolysis of proteid material by the proteolytic enzyme, as in the first case only 0.07 per cent. of the fats were hydrolysed, whilst in the last 96 per cent. were hydrolysed and carbon dioxide was formed. M. A. W.

Influence of Decomposition Products of Proteid Matter on the Saponification of Oils by Cytoplasm. EDOUARD URBAIN, L. PERRUCHON, and J. LANCON (*Compt. rend.*, 1904, 139, 641—643).—In a previous paper (preceding abstract) it has been shown that the formation of carbon dioxide during the germination of seeds is due to the decomposition of proteid matter, and the results of further experiments show that the total quantity of nitrogenous matter not precipitated by Weiss's method (compare Abstr., 1901, ii, 69) increases with the quantity of fatty substance saponified. In addition to carbon dioxide, the chief decomposition products of proteid matter in the process of the saponification of castor oil seeds are leucine and asparagine, and these substances in the presence of carbon dioxide or acetic acid exert an accelerating action on the saponification of the oil by cytoplasm (compare Effront and Schidrowitz, Abstr., 1903, ii, 680).

M. A. W.

The Assimilation of Carbon Dioxide. WALTHER LÖB (*Ber.*, 1904, 37, 3593—3596. Compare Euler, this vol., ii, 761).—Formaldehyde, which plays so important a part in the carbon assimilation of plants, has not been obtained as a product of the reduction of carbon dioxide by either chemical or electrolytic means. A repetition of the experiments of Berthelot (Abstr., 1901, ii, 2) and of Losanitsch and Jovitschitsch (Abstr., 1897, i, 179) showed that in the action of the silent electric discharge on dry carbon dioxide, carbon monoxide and ozone are produced, moist carbon dioxide yielding formic acid and hydrogen

peroxide. The process of carbon dioxide assimilation is endothermic, and the presence of a catalytic agent is probably essential in any attempt to imitate the natural process. C. H. D.

Decomposition of Carbon Dioxide by Light. ALEXIS BACH (*Ber.*, 1904, 37, 3985—3986).—A reply to Euler (this vol., ii, 761). A. McK.

Metabolism of Germinating Plants. ERNST SCHULZE and NICOLA CASTORO (*Zeit. physiol. Chem.*, 1904, 43, 170—198).—Experiments made on germinating lupins by the autolytic method confirm the previous conclusion that asparagine is a secondary product of proteid katabolism; the formation of arginine, a primary product, goes *pari passu* with proteid breakdown. W. D. H.

Action of some Salts and Monohydric Alcohols on the Development of Moulds. K. S. IWANOFF (*Centr. Bakt. Par.*, 1904, ii, 13, 139—144).—The toxicity of the metals of the uneven series of Mendeléeff's second group (Mg, Zn, Cd, Hg) increases with the atomic weight. This accords with the observations of others and with the results obtained with the alkali metals. Of other metals, manganese is the least toxic, then cobalt, nickel, and copper. The toxicity varies, however, to some extent according to the nitrogenous matter employed, and also according to the substance utilised as source of carbon.

The toxicity of primary monatomic alcohols increases with the length of the chain. Of the different butyl alcohols, *n*-butyl alcohol is the most poisonous. *n*-Propyl alcohol is more poisonous than *isopropyl* alcohol. Alcohols with double linkings are more poisonous than those with single linkings, as, for example, allyl alcohol and *n*-butyl alcohol.

Results obtained with copper accorded with Loeb's theory that the poisonous action consists in the combination of the metal with portions of the plasma. N. H. J. M.

Some Complex Carbohydrates. V. ZANOTTI (*Bied. Centr.*, 1904, 33, 660—663; from *Ricerch. Scuol. sup. Milan*, 1898—1902, 2, 15).—A substance was obtained from nut shells by treating with sodium hydroxide and precipitating with acetic acid and alcohol, which, when hydrolysed, yielded dextrose and xylose in constant proportions to each other. *Penicillium glaucum* yielded a substance from which mannose was obtained by hydrolysis.

The results of experiments in which purified cotton-wool was oxidised with potassium chlorate and hydrochloric acid, with chromic oxide and sulphuric acid, and with potassium permanganate and sulphuric acid were inconclusive; they indicate, however, that the cellulose is converted into substances containing less carbon or more oxygen. N. H. J. M.

Occurrence of Tyrosine in Elderberries (*Sambucus nigra*). J. SACK and BERNHARD TOLLENS (*Ber.*, 1904, 37, 4115).—The expressed juice of the elderberries, after precipitation of impurities

with lead acetate and hydrogen sulphide, yields on evaporation crystals of tyrosine. E. F. A.

Successive Conditions of Vegetable Matter. EUGÈNE CHARABOT and ALEXANDRE HÉBERT (*Compt. rend.*, 1904, 139, 608—609).—The results of experiments with *Ocimum basilicum*, *Citrus madurensis*, and *C. bigaradia* showed that the differences in solubility of the substances of the leaf and stem are similar to those in the essences (Charabot and Laloue, this vol., ii, 581). Roots and stems are formed of substances less soluble than those of the leaves. The diminished solubility of the substances of the stems is attributed partly to the production of woody matter and partly to the migration of soluble matters to new organs. In the case of the leaves, a continuous production of soluble matter compensates for the loss due to migration.

N. H. J. M.

Action of Various Insoluble Phosphates on Rice Plants. MUNESHIGE NAGAOKA (*Bul. Coll. Agr. Tōkyō*, 1904, 6, 215—261).—Rice was grown in wooden frames (0·8 sq. m.) and manured with ferric, ferrous, aluminium, and calcium phosphates respectively at the rate of 25, 50, and 100 kilos. of phosphoric acid per hectare, in addition to potassium and nitrogenous manures. The experiments extended over four years, but without further application of phosphates after the first year. The effect of the different phosphates over the whole period, compared with that of double superphosphate = 100, was as follows:

| | 1st year. | 2nd year. | 3rd year. | 4th year. |
|----------------------------|-----------|-----------|-----------|-----------|
| Double superphosphate..... | 100 | 100 | 100 | 100 |
| Ferric phosphate | 140 | 141 | 399 | 58 |
| Ferrous „ | 87 | 88 | 194 | 44 |
| Aluminium „ | 92 | 145 | 514 | 112 |
| Calcium „ | 117 | 110 | 161 | 118 |

The high results obtained the first year are attributed to the action of the large amount of humic acid in the soil on the phosphates.

Application of lime diminished the assimilability of the phosphates. Calcium carbonate, in conjunction with the largest amount of phosphates, had very little effect except in the case of ferric phosphate. The effect of calcium carbonate was, however, more lasting than that of lime.

N. H. J. M.

Behaviour of the Rice Plant to Nitrates and Ammonium Salts. MUNESHIGE NAGAOKA (*Bul. Coll. Agr. Tōkyō*, 1904, 6, 285—334. Compare Pagnoul, *Abstr.*, 1897, ii, 120; Klöpfer, 1900, ii, 616).—It is shown that paddy plants utilise nitrogen in the form of ammonium salts to a greater extent than nitrates, and this is attributed to the absence in the leaves of sufficient sugar for the conversion into proteids of all the nitrogen absorbed. It may also be due in part to denitrification and to formation of nitrites in the soil. Nitrous acid was detected in two cases.

The value of nitric nitrogen, as compared with ammoniacal nitrogen

= 100, was with paddy rice 40, with *Juncus* 37, and with arrow-head 33.

Results obtained with different nitrates (sodium, potassium, calcium, barium, strontium, and magnesium nitrates) showed that almost exactly the same amount of nitrogen was assimilated in each case (compare Schneidewind, *Jahresb. Agric. Chem.*, 1897, 20, 228). Differences in the relations of grain and straw were observed, but these are attributed to other conditions.

N. H. J. M.

Molasses Food from Seed-Beet Straw. W. ROSAM (*Bied. Centr.*, 1904, 33, 703—704; from *Oesterr.-ung. Zeit. Zuckerind. u. Landw.*, 1904, 32, 974).—The food is prepared by mixing equal weights of heated molasses and ground straw. It keeps well and is appreciated by cattle. In some cases, however, when the amount consumed was large (over 2 kilos.), eruptions were produced on the feet which healed slowly. The composition of the food was as follows: water, 19·86; proteids, 0·92; amino-acids, 5·64; fat, 0·28; sucrose, 25·20; non-nitrogenous extract, 19·87; crude fibre, 19·44; pure ash, 8·70; and sand, 0·09 per cent.

N. H. J. M.

Effects of Soil Ignition on the Availability of Phosphoric Acid for Rice Culture in Paddy Fields. MUNESHIGE NAGAOKA (*Bul. Coll. Agr. Tōkyō*, 1904, 6, 263—276).—The phosphoric acid soluble in hydrochloric acid of sp. gr. 1·15, ammonium citrate, acetic acid (5 per cent.), citric acid (1 per cent.), oxalic acid (1 per cent.), and carbonic acid (saturated) was determined in a soil before and after ignition. The ignited soil gave, in every case, more phosphoric acid than the original soil, owing to the liberation of phosphoric acid originally present in humus, nuclein, and lecithin (compare Nilson and Eggertz, *Abstr.*, 1890, 192; Schmoeger, *Landw. Jahrb.*, 1896, 25, and 1897, 26; Nannes, *Abstr.*, 1899, ii, 798, and Schreiber, *ibid.*, 1896, ii, 66).

The results of pot experiments with rice (manured with nitrogen and potassium) showed that the burnt soil gave very poor yields as compared with the unburnt soil, owing, probably, to deficiency of humus and to unfavourable mechanical conditions. A mixture of unburnt and burnt soil (3:1) gave, however, a much greater yield than unburnt soil alone.

Applications of lime, calcium carbonate, and potassium carbonate diminished the yield of rice, and still more the consumption of phosphoric acid; in most cases, the unfavourable action of the alkali continued the second year. It is desirable to add to burnt soil a certain amount of humus or organic matter which will yield humus.

N. H. J. M.

Organic Compounds of Phosphorus in the Soil. KEIJIRO ASO (*Bul. Coll. Agr. Tōkyō*, 1904, 6, 277—284. Compare preceding abstract).—The chief organic phosphorus compound in soils is nuclein; a very small amount of lecithin was found. The organic phosphorus is rendered available by burning the soil. Steam, under pressure, increased the solubility (in cold hydrochloric acid) of both phosphoric acid and sulphur.

N. H. J. M.

Influence of Liming on the Activity of the Phosphoric Acid of Manures. BERNHARD SCHULZE (*Bied. Centr.*, 1904, 33, 653—654; from *Fühling's Landw. Zeit.*, 1904, 53, 186, 216 and 261).—The phosphoric acid of bone-meal, when applied to soil poor in lime, is very nearly equal to citric-acid-soluble phosphoric acid. Liming has very little effect on water-soluble phosphoric acid, more on phosphoric acid soluble in citric acid, and most on bone-meal, when the phosphatic manure is put on in the spring. The greatest injury occurs when burnt lime is applied in the spring, and the least when calcium carbonate is applied in the autumn. In the case of sparingly soluble phosphates, the maintenance of a supply of humic acids is of importance.

N. H. J. M.

Influence of Liming on the Action of Phosphatic Manures. MUNESHIGE NAGAOKA (*Bul. Coll. Agr. Tōkyō*, 1904, 6, 195—214. Compare Kellner and Böttcher, *Abstr.*, 1901, ii, 275; 1902, ii, 351 and 528, and Söderbaum, this vol., ii, 78).—The experiments were made with rice grown in 57 wooden frames having an area of 0·8 sq. m. Various organic phosphatic manures (animal and vegetable) were applied, both without and with pure lime (at the rate of 400 kilos. per hectare).

The results showed that addition of lime greatly reduced the availability of the phosphoric acid, and that its action in conjunction with animal manures (fish, fish-bone, and steamed bone-meal) was twice as great as in the case of vegetable manures (rice, bran, rape, and other cakes). The effect of lime extends over the second year.

Animal phosphates were found to be much more active than vegetable phosphates; in the second year, the difference was less. The soil was a fine sandy loam containing 10—11 per cent. of humus and 0·9 per cent. of lime soluble in hot concentrated hydrochloric acid.

N. H. J. M.

Agricultural Employment of Calcium Cyanamide. MAX GERLACH (*Bied. Centr.*, 1904, 33, 649—651; from *Mitt. deut. Landw.-ges.*, 1904, St. 8. Compare Tacke, this vol., ii, 768).—Crude calcium cyanamide, prepared by heating powdered calcium carbide in air from which the oxygen has been removed, forms a black powder, resembling basic slag in appearance. It contains above 20 per cent. of nitrogen, readily soluble in water, calcium oxide and carbide, and carbon.

The results of pot experiments with barley and white mustard indicated that the manure is equal to sodium nitrate or ammonium salts. In field experiments extending over two years, the value of the manure proved to be much lower, 74 as compared with sodium nitrate = 100. In the case of some soils, especially peaty soils, the manure acts injuriously. This is probably due to the production of dicyanodiamide by the action of acids. Wagner showed that great loss of nitrogen, in the form of ammonia, may readily occur.

The nitrogen of calcium cyanamide can without difficulty be converted into ammonium sulphate.

N. H. J. M.

Analytical Chemistry.

Filter Stand. G. ILIOVICI (*Zeit. anal. Chem.*, 1904, 43, 508—509).—A light brass filter stand, capable of supporting six funnels, which, without the use of screws, can be fixed at any convenient height, and can also be moved sideways. The whole packs closely when taken to pieces. M. J. S.

The Use of Potassium Hydrogen Iodate for Standardising Volumetric Solutions. CHARLES E. CASPARI (*Pharm. Rev.*, 1904, 22, 371—376).—This salt may be prepared by mixing a solution of potassium hydrogen carbonate with an equivalent amount of iodic acid, and if the mixture then be neutral, a second quantity of iodic acid, equal to the first, is also added. The solution is evaporated until crystallisation begins and the first crop of crystals is rejected. The crystals which separate after the solution has cooled to 50° are almost pure and will be quite pure if recrystallised once from water. Potassium hydrogen iodate reacts with potassium iodide in acid solution according to the equation: $\text{KH}(\text{IO}_3)_2 + \text{IOKI} + 11\text{HCl} = 11\text{KCl} + 6\text{H}_2\text{O} + 6\text{I}_2$. One molecule of potassium hydrogen iodate is therefore equivalent to 12 molecules of sodium thiosulphate. The salt is readily reduced by a slight excess of sulphurous acid. After expelling the excess by heating, the solution, now containing hydriodic acid, may be used for standardising silver nitrate solutions. One molecule of potassium hydrogen iodate is equivalent to two molecules of silver nitrate. Finally, potassium hydrogen iodate may be employed to determine the strength of alkali solutions, using phenolphthalein as indicator, one molecule corresponding with one molecule of potassium hydroxide.

Potassium hydrogen iodate keeps well in solution. The salt contains no water of crystallisation, is neither deliquescent nor efflorescent, and can be dried at a temperature of 110° without decomposition taking place. W. P. S.

Detection of Fluorides in Meat Products. J. FROIDEVAUX (*Ann. Chim. anal.*, 1904, 9, 383).—Thirty grams of the comminuted sample are moistened with 2 c.c. of a saturated solution of sodium carbonate and heated until the organic matter is completely destroyed. The charred mass is then powdered and boiled with water. The filtrate is concentrated and strongly acidified with hydrochloric acid, a few drops of heliantin are added, and then solution of ammonium acetate until the liquid turns yellow. To the liquid, which now contains free acetic acid, is added solution of calcium chloride which, in the presence of an alkali fluoride, will cause a more or less heavy precipitate of calcium fluoride.

The precipitate is then collected and submitted to the usual test with silica and sulphuric acid in Sanglé-Ferrière's apparatus.

L. DE K.

Estimation of Fluorine in Wine and Beer. FREDERICK P. TREADWELL and ARTHUR A. KOCH (*Zeit. anal. Chem.*, 1904, 43, 469—506).—The use of sodium fluoride (under the trade name "Remarcol") as a preservative for sweet wines and beer having apparently been followed by toxic symptoms, a commission of chemists has undertaken the investigation of the available methods for the estimation of fluorine in those beverages. Preliminary experiments showed that the solubility of ignited calcium fluoride in water amounted to 0.0016 gram, and in $3/2N$ acetic acid to 0.0111 gram per 100 c.c. Although slightly volatile at the temperature of the blow-pipe, it is practically non-volatile at that of the Bunsen burner. In the examination of wine, in cases where the fluorine present is sufficient to yield 5 mg. of calcium fluoride per 100 c.c., Brand's method (*Abstr.*, 1896, ii, 447) can therefore be employed quantitatively. Quantities down to 1 mg. per 100 c.c. can be detected by that method, but the quantitative errors are large with such small amounts. The results are not affected by the presence of sulphates or of sugar. Phosphates and tartrates must, however, be separated. The modified method adopted is as follows: 100 c.c. of the wine are made feebly alkaline with sodium hydroxide (not with carbonate, for the escaping carbon dioxide carries off hydrogen fluoride); silver nitrate is then added as long as it produces a precipitate, the mixture is made up to 250 c.c. and filtered; 200 c.c. of the filtrate are treated with an excess of sodium chloride, made up to 250 c.c., shaken, and left at rest for 24 hours; 175 c.c. of the clear solution are treated with 3—4 c.c. of $2N$ sodium carbonate solution, precipitated with a large excess of calcium chloride, and boiled for 5 minutes. The precipitate is collected on a filter, washed thoroughly with hot water, ignited at a dull red heat for 10—20 minutes, then digested with 2—4 c.c. of $3/2N$ acetic acid, washed free from calcium acetate, ignited, and weighed. The treatment with acid, &c., is repeated until a diminution of less than 0.5 mg. takes place. For each 100 c.c. of filtrate and washings, 0.0016 gram is added to correct for solubility. Ten specimens of genuine wine did not contain enough fluorine to allow of its detection in 100 c.c. Fluorides are therefore not normal constituents of wine. One sample of guaranteed purity showed 5.4 grams of sodium fluoride per hectolitre.

The above method is unsuitable for beer. A modification of Penfield's method (*Abstr.*, 1879, 829) gave results which were fairly concordant, but about 6 per cent. too low. This loss was traced to the incineration which was necessary to free the calcium fluoride from organic matter. The best results were obtained with a special form of reaction vessel in which the contact of the calcium fluoride with the sulphuric acid was promoted by the current of air. The beer must be made alkaline with sodium hydroxide, since otherwise the precipitate will contain calcium hydrogen phosphate, which during the ignition will decompose part of the calcium fluoride. In nine samples of beer examined, no fluorine could be detected. M. J. S.

New Method for the Estimation of Sulphur in Irons and Steels. H. B. PULSIFER (*Chem. News*, 1904, 90, 230—231).—2.5

grams of the sample, preferably in the form of drillings, are moistened in a beaker with a little water and then treated with 20 c.c. of chloric acid of sp. gr. 1.12, a very small quantity of hydrofluoric acid being also added. When the action has subsided, 5 c.c. of concentrated hydrochloric acid are added and the mixture boiled to dissolve any particles on the sides of the beaker. The solution is now poured on a filter and the latter washed once or twice with water. To the filtrate, 20 c.c. of concentrated hydrochloric acid are added and the whole evaporated to a volume of about 10 c.c. The filter and residue are meanwhile placed in a nickel crucible, covered with sodium peroxide, and heated over a strong flame. The cover of the crucible should be held down by the tongs. In a few seconds, the fusion is completed. After cooling, the fused mass is cautiously dissolved in water, the solution acidified with hydrochloric acid, filtered, and the filtrate added to the main portion already obtained. The united filtrates should have a volume of about 100 c.c., and are precipitated with barium chloride as usual.

W. P. S.

Applicability of Phosphorous Acid for the Estimation of Selenium and Tellurium. ALEXANDER GUTBIER (*Zeit. anorg. Chem.*, 1904, 41, 448—451).—Compounds of hexavalent selenium or tellurium, such as selenic and telluric acids, cannot be completely reduced by phosphorous acid. Selenious and tellurous acids are very readily reduced to the corresponding elements when their concentrated solutions in hydrochloric acid are boiled with phosphorous acid. The method is quantitative.

A. McK.

Estimation of Nitrogen. EDUARD JALOWETZ (*Chem. Centr.*, 1904, ii, 1068; from *Allgem. Zeit. Bierbrau. u. Malzfabr.*, 1904).—The author calls attention to the considerable amount of alkalis which may be dissolved from the glass condenser during an ammonia estimation by Kjeldahl's method, and find their way into the distillate, thus vitiating the result.

L. DE K.

Influence of the Quality of the Glass on the Accuracy of the Nitrogen Estimations by Kjeldahl's Method. K. BARELT and H. SCHÖNEWALD (*Chem. Centr.*, 1901, ii, 1068; from *Woch. fur Brauerei*, 21, 523).—The authors confirm Jalowetz's statement as to the solubility of alkalis from the glass (see preceding abstract). It is recommended to steam the apparatus well before use, and not to continue the distillation longer than is strictly necessary.

L. DE K.

Gravimetric Estimation of Boric Acid by Extraction with Ether. ALFRED PARTHEIL and J. A. ROSE (*Arch. Pharm.*, 1904, 242, 477—488. Compare Abstr., 1902, ii, 48).—Boric acid cannot be weighed as metaboric acid, for when it is dried at 105° a little boric acid volatilises with the water. When a solution of boric acid in anhydrous ether is evaporated, no acid volatilises, as is the case when the ether contains even a little water. At 25°, 100 grams of anhydrous

ether dissolve 0.00775 gram, 100 grams of ether saturated with water 0.2391 gram, of boric acid, H_3BO_3 . The distribution ratio of boric acid in ether saturated with water : water saturated with ether is 1 : 45.4 at 26°, 1 : 44.6 at 17°.

Boric acid in milk was estimated by evaporating 50 c.c. with 1 gram of anhydrous sodium carbonate, igniting the residue, extracting the ash with water, making the extract faintly acid with hydrochloric acid, precipitating the phosphoric acid with a few drops of ferric chloride solution, removing the excess of iron with alkali hydroxide, filtering, concentrating the filtrate to 10—15 c.c., acidifying with hydrochloric acid, extracting with ether, &c.; the error in 3 estimations lay between 0 and +10 per cent.

Boric acid in minced meat was estimated by adding 1 gram of anhydrous sodium carbonate to 20 grams of the meat, drying, igniting the residue cautiously, and treating the ash as in the preceding case; the error in 3 estimations was -0 to +0.5 per cent.; in a commercial sample, 0.378 per cent. of boric acid was found.

Borax in margarine was estimated by melting 50 grams of the sample 4 times in succession with 20 c.c. of water, the water being poured off each time after the fat had solidified. The water was then made alkaline and evaporated to dryness, the residue ignited, the ash extracted with water, the extract acidified with hydrochloric acid, extracted with ether, &c. In a commercial sample, 0.154 per cent. of borax was found.

C. F. B.

The Preparation of Alcoholic Solutions of Potassium Hydroxide which will remain Colourless. HERMANN THIELE and ROBERT MARC (*Zeit. öffentl. Chem.*, 1904, 10, 386—387).—To prepare 1 litre of $N/2$ solution, 43.5 grams of potassium sulphate are mixed with 110—120 grams of barium hydroxide in a platinum or china basin and 100 c.c. of water are poured over the mixture. The basin and its contents are weighed, heated for 15 minutes with constant stirring, cooled, and again weighed. Water is then added until the original weight is obtained. The contents of the basin are now rinsed into a flask with 800 c.c. of alcohol and a further 100 c.c. of water. After shaking and allowing the precipitate to settle, 3 or 4 c.c. of concentrated potassium sulphate solution are added to remove any barium hydroxide dissolved by the 80 per cent. alcohol. When the precipitate has again settled, the clear supernatant solution may be drawn off. The latter will be of approximately the desired strength and will keep for months without turning brown.

W. P. S.

Estimation of Silver in Commercial Zinc. K. FRIEDRICH (*Zeit. angew. Chem.*, 1904, 17, 1636—1644).—200—1000 grams of the granulated sample are treated with hydrochloric acid, and when practically all dissolved, the residue is collected, washed, and melted with 7.5—15 grams of assay lead with addition of some borax. The regulus is then cupelled in the usual way and the button of silver examined as usual for traces of gold.

A table is given showing the percentage of silver in 31 samples of commercial crude and refined zincs.

L. DE K.

Strontium Chromate and the Microchemical Detection of Strontium. WILHELM AUTENRIETH (*Ber.*, 1904, 37, 3882—3887).—Strontium is most readily detected microchemically by the formation of the chromate, which forms bundles of long, slender, highly refracting needles, or, on separating from very dilute solutions, thick prisms of hexagonal habit. The latter form appears to be labile, and is slowly transformed into the former. Under the same conditions, barium chromate separates in an amorphous form or in indefinite crystals, and calcium chromate remains in solution. Strontium chromate dissolves readily in acetic acid. When calcium, strontium, and barium are present together, they are best detected by separating the anhydrous chlorides by means of absolute alcohol, and subsequently applying the microchemical test. C. H. D.

Estimation of Metallic Aluminium in Aluminium Powder. E. KOHN-ABREST (*Ann. Chim. anal.*, 1904, 9, 381—382).—0.5 gram of the powder is heated with 20 grams of ferric sulphate and 50 c.c. of water in a current of carbon dioxide until dissolved. When cold, the liquid is mixed with 20 c.c. of sulphuric acid, diluted to 250 c.c. with water, and the ferrous iron formed is then at once titrated with permanganate. One part of iron equals 0.1607 part of aluminium.

Should the powder contain iron, this must be estimated and allowed for, as it also causes reduction. L. DE K.

Standardisation of Potassium Permanganate. H. CANTONI and M. BASADONNA (*Ann. Chim. anal.*, 1904, 9, 365—371).—The authors come to the conclusion that the iodometric process should be used in laboratories where no facilities exist for the preparation of electrolytically-deposited metallic iron (compare Dupré, this vol., ii, 591). L. DE K.

Volumetric Estimation of Chromium and Iron simultaneously present. B. GLASMANN (*Zeit. anal. Chem.*, 1904, 43, 506—508).—Ferric iron is reduced by sulphurous acid, which has no action on chromic salts, and is titrated in the usual way with permanganate. The same portion of solution, which should not contain more than 0.05 gram of Cr_2O_3 , is then treated with zinc and sulphuric acid, by which the chromic oxide is reduced to chromous oxide. A second titration with the permanganate reoxidises both ferrous and chromous oxides to ferric and chromic, and the latter is calculated from the difference between the two titrations. M. J. S.

Colour Reaction for Tungsten. C. FRABOT (*Ann. Chim. anal.*, 1904, 9, 371—372).—The tungstic acid, which may contain an admixture of silica but must be free from molybdic acid, is mixed with a few crystals of uric acid and then with a few drops of aqueous sodium hydroxide, when a fine blue colour will be developed. L. DE K.

A New Reaction for Bismuth. C. REICHARD (*Chem. Zeit.*, 1904, 28, 1024—1026).—A concentrated solution of bismuth chloride gives

a dark red coloration with an excess of brucine. The colour is not destroyed on adding a drop of hydrochloric acid and evaporating to dryness. This reaction is characteristic for bismuth, but antimony also gives a similar reaction on applying heat. L. DE K.

New Reaction of Formic Acid. EZIO COMANDUCCI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1904, [iii], 10, 202—203).—With a cold concentrated aqueous sodium hydrogen sulphite solution, formic acid, even in aqueous solutions of 0.5 to 1 per cent. strength, gives a pale yellow coloration, which becomes orange-yellow on boiling the liquid for a few seconds, and disappears on further heating.

This test may be employed to detect from 1 to 1.5 per cent. of the acid in formalin, methyl alcohol, glycerol, or acetic acid. It is best carried out by diluting about 2.5 c.c. of the liquid to be tested with an equal volume of water, adding 15 drops of concentrated sodium hydrogen sulphite solution (5 grams to 5 c.c. of distilled water), agitating, and heating gently. T. H. P.

Indirect Estimation of Fat in Milk. L. PIERRE (*Ann. Chim. anal.*, 1904, 9, 390).—A further reply to Steinmann (this vol., ii, 789). L. DE K.

The Acidity of Milk. R. HANNE (*Milch Zeit.*, 1904, 33, 659—660).—The author recommends the following modification of Soxhlet's method for the estimation of the acidity of fresh milk. To 50 c.c. of the milk are added 2 c.c. of a 2 per cent. alcoholic phenolphthalein solution, and the mixture is titrated with *N*/10 sodium hydroxide solution. The end-point of the titration is taken when a permanent red coloration is obtained. The number of c.c. of *N*/10 sodium hydroxide required to neutralise the 50 c.c. of milk is termed the acid value of the milk. One "degree" of acidity as estimated by Soxhlet's method therefore corresponds with 1.25 "degrees" by the above method. Water should not be added to the milk before titration, and the author sees no advantage in calculating the acidity on 100 c.c. of milk. The addition of 3 drops of formalin to the 50 c.c. of milk caused an increase in the acidity, which was not due to the acidity of the formalin. W. P. S.

Reactions for the Microchemical Detection of Organic Bases. THEODORE H. BEHRENS (*Zeit. anal. Chem.*, 1904, 43, 333—355. Compare Abstr., 1903, ii, 455).—A solution of iodine in potassium iodide serves to distinguish between fatty and aromatic bases, yielding crystalline derivatives with the latter only. Aromatic bases do not form double magnesium phosphates, it is therefore possible to separate them from ammonia and most of the alkylamines by the addition of magnesium hydroxide and sodium phosphate. Heterocyclic bases may be detected in the presence of homocyclic bases by oxidising the latter with chromic acid.

A method for the separation of primary, secondary, and tertiary aromatic bases by means of benzenesulphonic chloride is described.

Tertiary bases also yield sparingly soluble compounds with potassium ferrocyanide and hydrochloric acid.

Homocyclic diamines are separated from monoamines by their non-volatility in a current of steam, or, in many cases, by the formation of sparingly soluble sulphates.

Aminophenols, imines, and amino-acids are separated by ammonium carbonate, which sets free the two former, the amino-acids remaining as ammonium salts. Imines are separated from aminophenols by precipitation with sodium acetate; aminophenols and hydroxyquinolines yield brightly coloured compounds with diazobenzenesulphonic acid.

The orientation of bases in the aniline, aminophenol, and naphthylamine groups may be determined, and a partial separation of the isomerides effected by adding a cold saturated solution of potassium antimony tartrate to a neutral solution of the hydrochlorides. The characters of the ortho-, meta-, and para-derivatives are described.

Homocyclic Amines.—The aqueous solution is very slowly distilled with sodium hydroxide. The first drops of the distillate contain only aniline, followed by the toluidines. These are precipitated as iodo-sulphates by adding iodine and sodium sulphate to the acidified solution. The xylienes separate as hydriodides. The higher homologues and α -naphthylamine separate in the solid form, β -naphthylamine mostly remains in the distilling flask. Phenylenediamines are extracted from the residue by adding potassium carbonate and shaking with *isobutyl* alcohol. *o*-Phenylenediamine is precipitated by alloxan and sodium acetate as quinoxaline; the *p*-diamine is precipitated from the filtrate as sulphate; the *m*-diamine is recognised by its colour-reactions on diazotising or by its iodo-derivative.

Formyl and acetyl derivatives of bases yield characteristic platinum-iodides.

Benzylamines.—The free bases are shaken with water and a small quantity of benzene, which extracts di- and tri-benzylamine (1). Sodium hydroxide is added to the residual solution, and the mono-benzylamine extracted with benzene and precipitated with α -naphthaquinone. The benzene solution (1) is evaporated, converted into sulphates, and shaken with benzene after addition of sodium carbonate. A crystalline residue on evaporating the benzene indicates tribenzylamine.

Heterocyclic Bases.—Pyridine and its homologues are separated from a solution in which litmus remains violet by distillation. Pyridine is precipitated as tri-iodopyridine, the homologues are separated by oxidation with potassium permanganate. Pyrrole and indole may be distilled even in presence of free sulphuric acid. Quinoline derivatives are characterised by their ferrocyanides. Hydroxyquinolines are not volatile in a current of steam. Aminoquinolines react both as quinoline derivatives and as primary amines. Acridines are separated from quinoline by precipitation as acridine sulphite, and may also be recognised by their crystalline mercurichlorides.

Alkaloids.—Most of the alkaloids may be characterised by their ferrocyanides. Coniine, nicotine, and sparteine distil in a current of steam. Pilocarpine, cytisine, cocaine, ecgonine, and the atropine group dissolve readily in water and may be sublimed. To separate

them, sodium carbonate is added to the solution, from which light petroleum extracts cocaine; benzene then extracts pilocarpine, tropine, atropine bases, and codeine; chloroform extracts cytisine; eegonine is extracted last by *isobutyl* alcohol. Morphine, apomorphine, and cupreine are sparingly soluble in water, dissolve in sodium hydroxide, and are precipitated by ammonium carbonate. Narceine, narcotine, papaverine, and thebaine are precipitated by sodium carbonate, and do not dissolve in sodium hydroxide. Strychnine cannot be separated perfectly from brucine, the best results are given by precipitation with platinic chloride. Veratrine (cevadine) yields no characteristic precipitates. The cinchona bases may be fractionally sublimed, the first fraction containing cinchonine and cinchonidine, which are then separated by crystallisation from water. The second fraction, containing quinine and quinidine, is separated with difficulty. Different methods are described according to the relative proportions of the various cinchona bases present.

The microscopic characters of the various precipitates are described.
C. H. D.

Alkaloid Reactions. III. Atropine. C. REICHARD (*Chem. Zeit.*, 1904, 28, 1048—1050).—The following new tests for atropine are given. If atropine sulphate is rubbed with a little sucrose and moistened with a drop of hydrochloric acid, the mass turns rose-red or dark red on warming and remains so for some time. If atropine is mixed with arsenious or arsenic acid and sulphuric acid, a reduction of arsenic takes place. If a small particle of cobalt nitrate is dissolved in a drop of water and mixed with a trace of atropine sulphate, no reaction takes place in the cold, but, on warming and evaporating, a green residue is obtained, which dissolves in water with a green colour; at the same time, the characteristic atropine odour is noticed. This colour is destroyed by ammonia, potassium hydroxide turns it violet. A solution of bismuth trichloride gives no reaction with atropine, but, on adding sulphuric acid, an intense yolk-of-egg colour is obtained. A solution of antimony trichloride gives a green colour on warming. Other reactions of less importance are also communicated.
L. DE K.

Certain Reactions of the Cinchona Alkaloids. ALBERT B. LYONS (*Pharm. Rev.*, 1904, 22, 365—371).—A slightly acid solution containing about 2 per cent. of quinine sulphate gives precipitates when mixed with a 10 per cent. solution of either ammonium acetate, ammonium citrate, potassium sodium tartrate, ammonium oxalate, or sodium salicylate. A similar solution of cinchonidine sulphate is also precipitated by these reagents with the exception of ammonium oxalate. Sodium salicylate alone precipitates quinidine and cinchonine from their acid solutions. Borax gives no precipitate with any of these alkaloids if the solutions be distinctly acid in reaction, whilst sodium benzoate precipitates all four; the addition of a little water, however, redissolves the crystals. Sodium phosphate precipitates quinine, cinchonidine, and cinchonine, but not quinidine. Potassium iodide and chromate do not precipitate these alkaloids in acid solu-

tions. In neutral solutions, precipitates are obtained in the case of quinine. Acid solutions of quinine are not affected by resorcinol, but strong neutral solutions of quinine bisulphate deposit crystals when mixed with the latter reagent. In all cases where precipitation occurs, the addition of more sulphuric acid or a little alcohol redissolves the precipitate.

W. P. S.

Tests for Strychnine and Brucine. [II. Strychnine.] C. REICHARD (*Chem. Zeit.*, 1904, 28, 977—979).—A critical review of tests already known. The following new reactions are given. A mixture of strychnine nitrate and copper nitrate yields a residue which turns violet on addition of stannous chloride, but, on drying, the mass again becomes green. On evaporating strychnine nitrate with platinic chloride and then adding sulphuric acid, the mixture turns dark red on warming; brucine turns yellow. Hydrogen peroxide, strychnine, and sulphuric acid give a blue liquid with yellow edges; after a while, the mixture turns yellow; the colouring matter is not extracted by ether. Sulphuric acid, strychnine, and titanic acid give a blue liquid gradually changing to yellow, which remains so on adding water (distinction from brucine). Strychnine, when evaporated with potassium hydroxide, gives a residue which turns dark blue on adding stannous chloride; brucine gives no colour. Hydrochloric acid and potassium persulphate give no reaction with strychnine in the cold, whilst with brucine a splendid red colour is developed which disappears only after some time. On warming, the strychnine solution turns yellow. This persulphate test will show the smallest admixture of brucine in a strychnine solution.

L. DE K.

The Neutral-red Reaction for Bacillus Coli Communis. ERNEST W. MOORE and CECIL REVIS (*J. Pathol. Bacteriol.*, 1904, 10, 97—104).—Unsatisfactory results were obtained in the use of this reaction; this is due to the kind of medium used; the addition of glucose is inhibitory rather than the reverse. The presence of lactose appears to be essential.

W. D. H.

Reactions of the Oxidising Enzymes of Cow's and Human Milk. FRANZ UTZ (*Chem. Centr.*, 1904, ii, 1000; from *Oesterr. Chem. Zeit.*, 1904, 7, 389—391).—An adverse criticism of Rullmann's work (this vol., ii, 304).

L. DE K.

Detection of Yeast Extract in Meat Extract. M. WINTGEN (*Arch. Pharm.*, 1904, 242, 537—538).—A 10 per cent. solution of the extract is made, and 20 c.c. of it are mixed with 2 c.c. of sulphuric acid (1 : 4) and salted out with powdered zinc sulphate. After remaining for 1—2 days, the liquid is filtered through a good filter, the first few c.c. that come through being poured back on to the filter; if not less than 20—30 per cent. of the extract was yeast extract, the filtrate is milky. This turbidity must be looked for at once, for it disappears gradually when the filtrate is allowed to remain. Milk extracts, like meat extracts, give a perfectly clear filtrate in the same circumstances.

C. F. B.